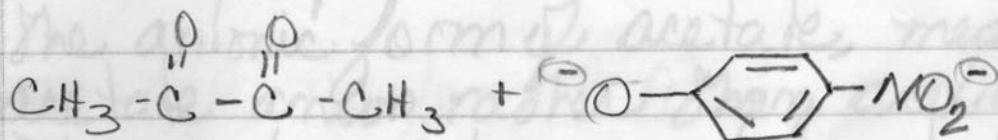
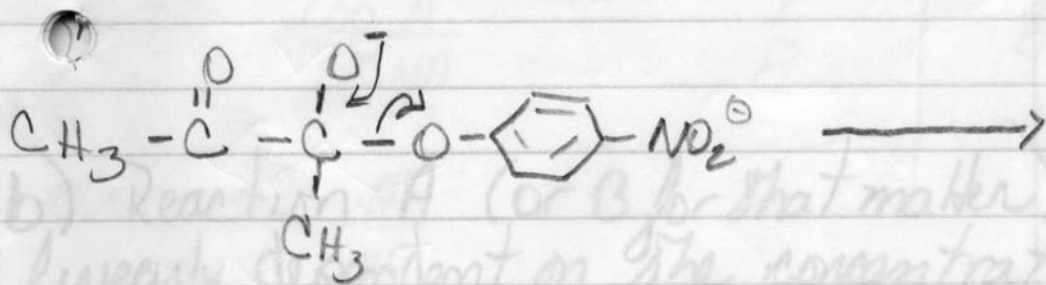
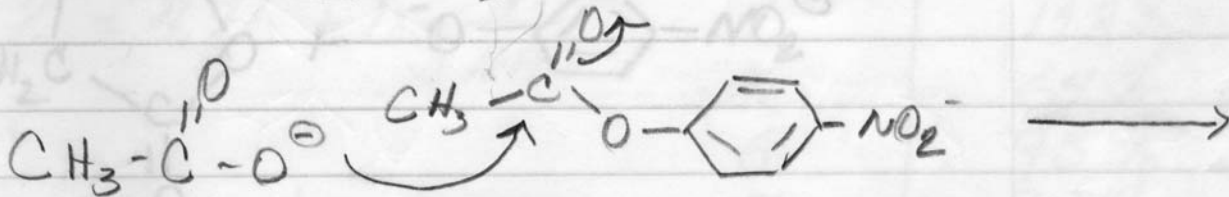


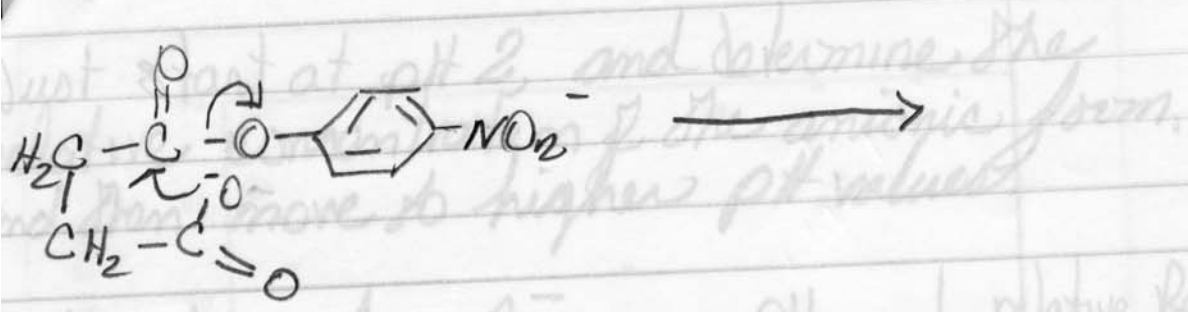
a) Reaction a is a bimolecular reaction. It proceeds with a second order rate constant $k_2 = 4 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$.



Reaction b is a unimolecular reaction. It proceeds with a first order rate constant $k_1 = 0.8 \text{ s}^{-1}$.



$\frac{1}{2} \times \frac{1}{1000}$



pH = pKa + log $\frac{A^-}{HA}$	pH	relative Rate
	2	0.174
	3	1.7%
	4.76	14.8%
	5	64%
	6	95%
	7	99%
	8	99.9%

b) Reaction A (or B for that matter) is linearly dependent on the concentration of the anionic form of acetate, meaning acetate anion rather than acetic acid. The reaction is base catalyzed, because base removes the proton from acetic acid. It deprotonates it. From the Henderson-Hasselbalch equation, you know that at pH = 4.76, the concentration of the anionic form is equal to the concentration of the protonated form.

Just start at pH 2, and determine the relative concentration of the anionic form, and then move to higher pH values.

pH	relative Rate
2	0.174
3	1.7%
4	14.8%
5	64%
6	95%
7	99%
8	99.9%

$$\text{pH} = \text{pKa} + \log \frac{A^-}{HA}$$

$$2 = 4.76 + \log \frac{A^-}{HA}$$

$$-2.76 = \log \frac{A^-}{HA}$$

$$0.00174 = \frac{A^-}{HA}$$

HA = 1 - A, Therefore, $\frac{A^-}{1 - A} = 0.00174$

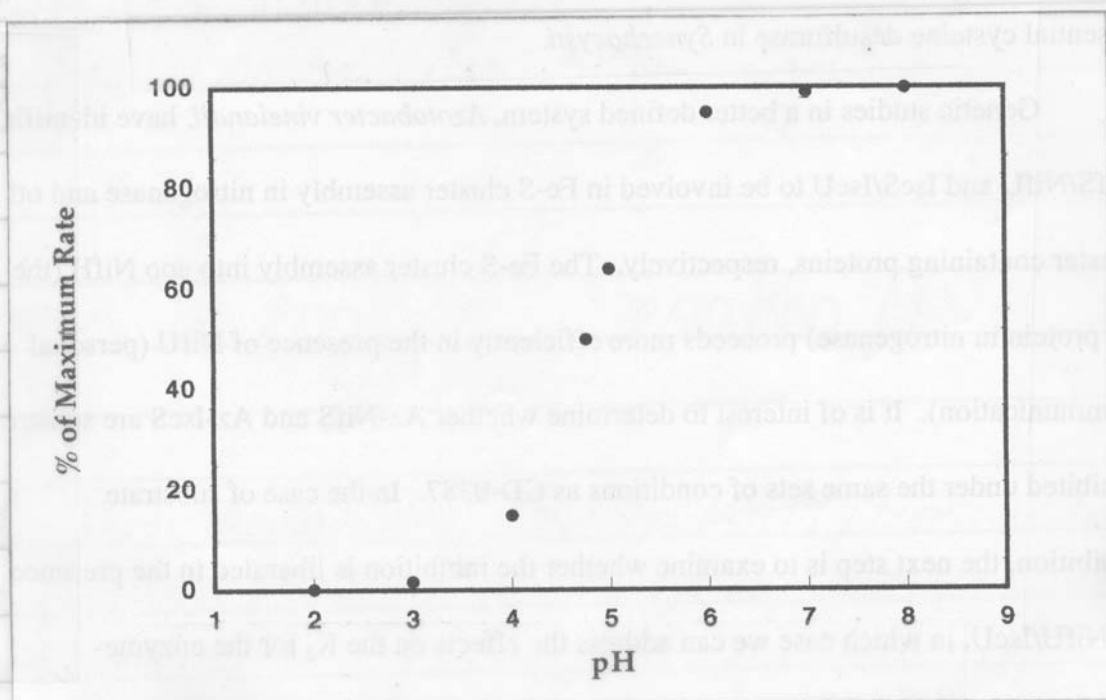
$$A^- = 0.00174 - 0.00174A$$

$$1.00174A^- = 0.00174$$

$$A^- = 0.00174$$

$$= 0.174\% \text{ Max}$$

Perform above calculations at other pH values and plot graph.



c) As described above, reaction A has a second order rate constant. Reaction B has a first order rate constant.

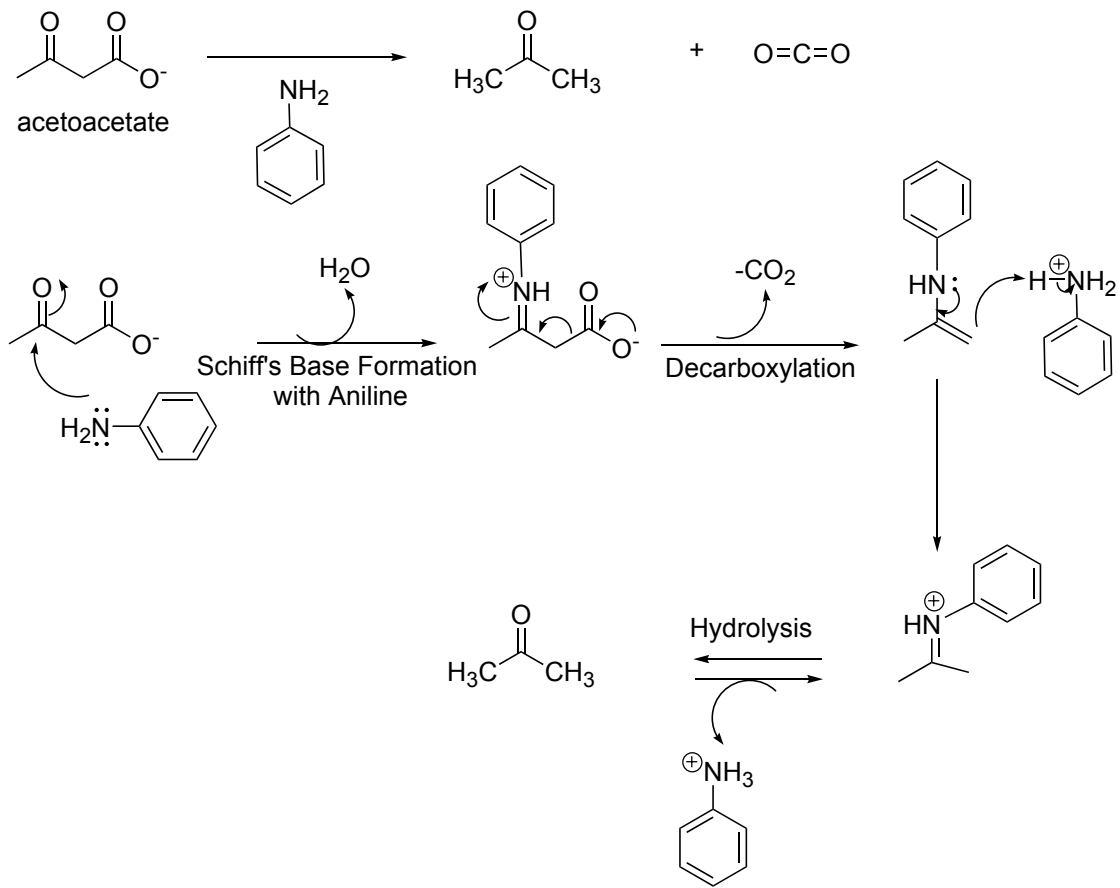
d) The effective concentration in Reaction B refers to the concentration of acetate in reaction A that would yield a first order rate constant in reaction A of equal magnitude of that of reaction B.

$$\text{effective concentration} = \frac{k_1}{k_2} = \frac{0.8 \text{ s}^{-1}}{4 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}}$$

$$= \frac{200,000}{\text{M}^{-1}} = 200,000 \text{ M}$$

As you can see, this concentration is ridiculously high. Therefore, for various reasons, having the nucleophile tethered to the electrophile, is like running the reaction in 200,000 M water.

Problem 10.



Problem 6

