CML 103 (2021) Final

Part 1 (Marks 15)

(1) An enzyme (E) has K_M = 5 uM and k_{cat}=210 s^{-1} for substrate S_1.

(a) Calculate the initial rate of reaction (V) when concentration of substrate is 10 μM and total enzyme concentration is 0.1 μM. (2)

(b) The presence of 6 mM of an uncompetitive inhibitor (I) decreased the initial rate by a factor of 2. What is the value of K_{ESI} (3)

(c) A competitive inhibitor S_2 is simultaneously present in the solution ($[S_1]$=10 μM, $[S_2]$= 10 μM, $[E_0]$=10 μM, [I]=0). If K_M=10 μM and k_{cat}=100 s^{-1}, calculate V_B/V_A? (2)

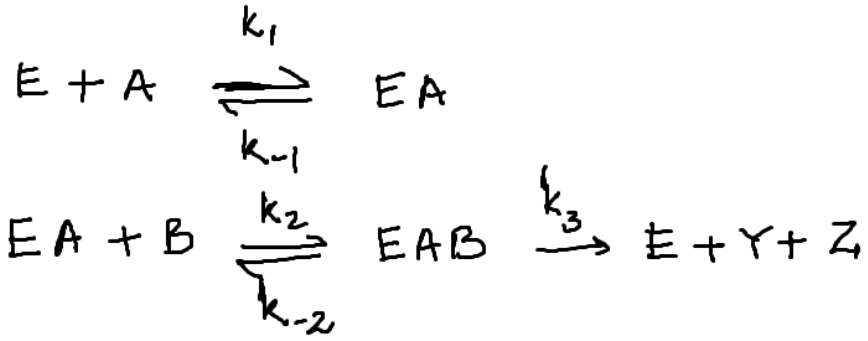
(2) The rate of reaction between ethylene and hydrogen on Nickel surface is given by:

by

$$v = \frac{k[H_2][C_2H_4]}{(1 + K[C_2H_4])}$$

Propose the mechanism of addition of hydrogen on ethylene on two different surfaces with appropriate reasoning? (4)

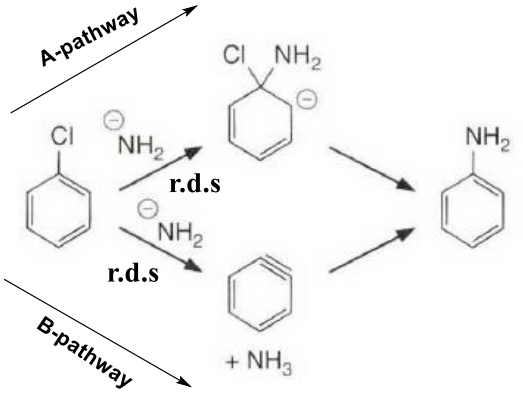
(3) An enzyme, E, reacts with substrate A and B by following mechanism:



Derive an expression for the steady state concentration of EAB and d[P]/dt in terms of total concentration of enzyme, $[E_0]$, [A], [B], rate constants k_1, k_{-1}, k_2, k_{-2} and k_3 (Remember that $[E]_0$=[E]+[EA]+[EAB]. [4]

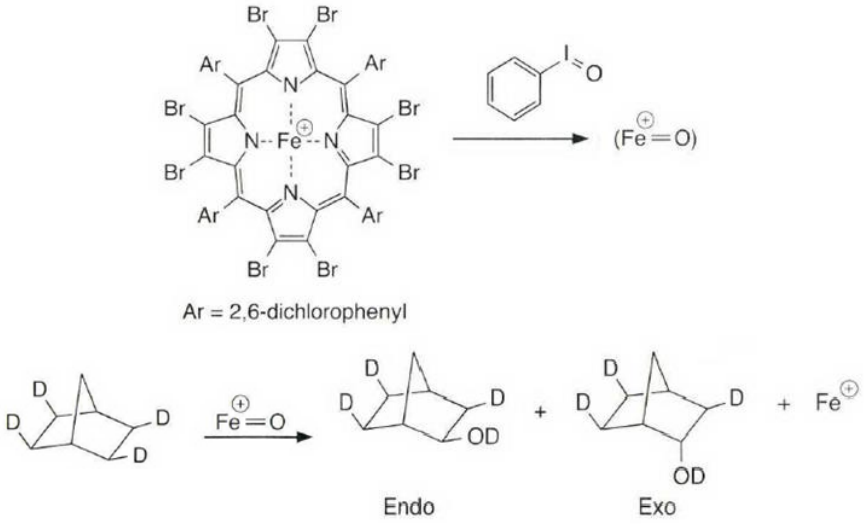
Part-2 (Total Marks: 40)

1. The treatment of chlorobenzene with potassium amide in liquid ammonia results in the formation of aniline. Propose **minimum three experiments** you can devise, that can be used to distinguish between the two mechanisms given below. **Explain each experiment** how it can distinguish one pathway compared to the other pathway. (6)

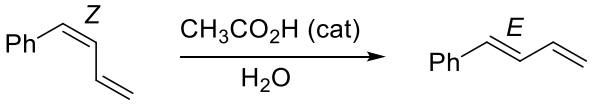


2. The hydroxylation of deuterionorbornane catalyzed by the following iron-oxo complex gives
a) A mixture of endo- and exo-norboran-2-oIs is produced
b) Shows a primary kinetic isotope effect of (k_H/k_D) = 5

What mechanism might account for this? (3)

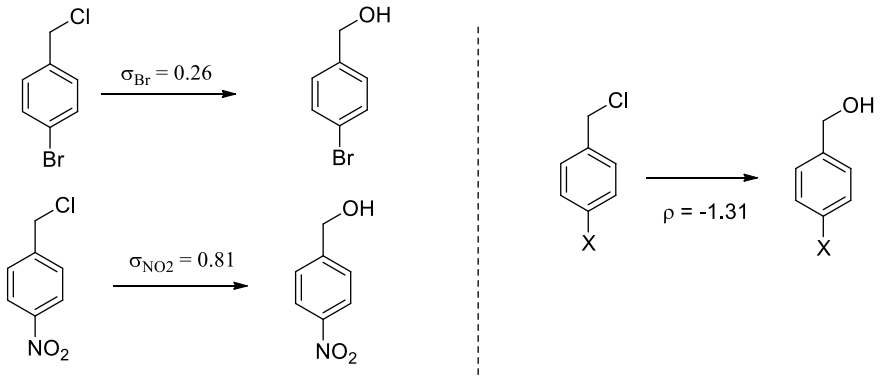


3. Q. The following reaction occurs by a general-acid catalyzed mechanism. Propose a mechanism for this reaction (**draw every step clearly and cite the rate determining step**). Propose minimum three experiments you can devise to support your proposed mechanism. (3+3)

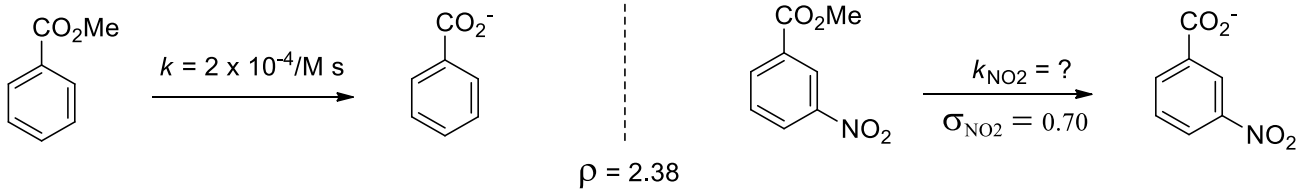


4. Q. The acid-catalyzed hydrolysis of substituted ethylbenzoates has a ρ value of 0.14, whereas the base-catalyzed hydrolysis of the same series of compounds shows a ρ value of 2.19. Why is there such a difference? **Explain with mechanisms** (3)

5. Q. Determine the value of $k_{p\text{-}Br}/k_{p\text{-}NO2}$. **Show detailed calculation**. (4)
Which reaction is faster? (1)

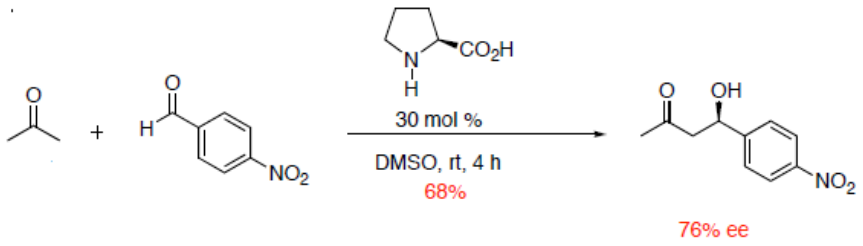


6. Q. What is the value of k_{NO2}? (3)

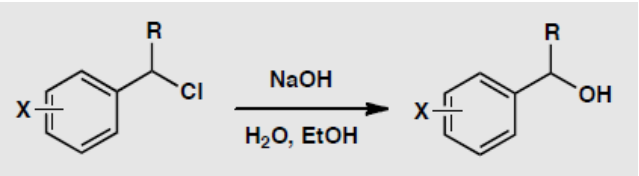


ρ = 2.38

7. Draw the mechanism of the following reaction. Show every step clearly. (4)



8.Q. Explain the difference between these Hammett ρ values by **drawing mechanisms** for the two reactions. In both cases the ring marked with the substituent X is varied.
When R = H, ρ = –0.3 but when R = Ph, ρ = –5.1. (4)



9. Q. The hydrolysis of the following acyl chloride displayed a non-linear Hammett plot. Draw the **possible mechanisms** of the hydrolysis reaction and **assign the rate determine step** that follows this non-linear Hammett plot. (6)