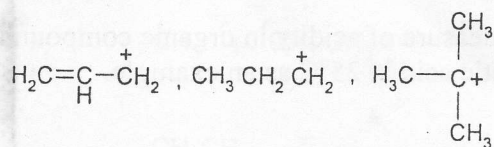


Eastern University, Sri Lanka
First Year First Semester Examination in Science
2008/2009 (Oct. / Nov. 2010)
CH 104 Reaction Mechanisms and Chemical Kinetics
(Proper and Repeat)

Answer all questions

Time: One hour

1. a. (i) Arrange the following carbocations in the increasing order of stability. Give reason for your answer.

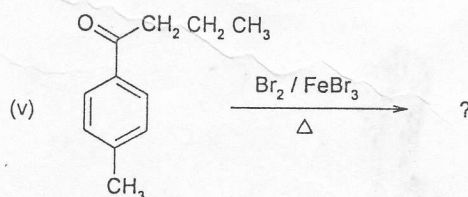
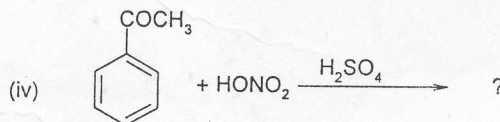
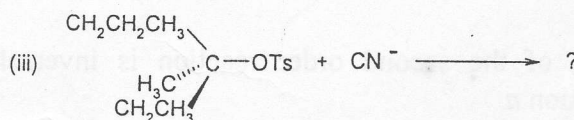
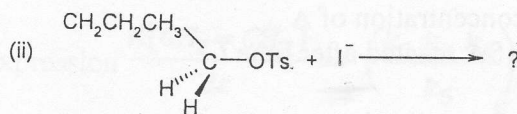
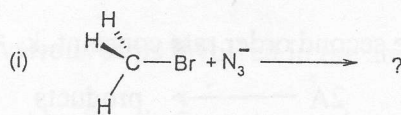


(10 marks)

(ii) Draw the relative energy position of all the resonance structures of 1,3-butadiene. Give reason indicate the major contributor and the minor contributor to the resonance hybrid.

(10 marks)

b. Identify the structure of the product(s) that could be obtained in each of the following reaction



(20 marks)

c. (i) Write down the mechanism of nitration of benzene. (10 marks)

(ii) Draw a fully labelled energy profile diagram for the above reaction. (15 marks)

(iii) Would you expect any change in the reactivity if C₆D₆ (deuterated benzene) is used instead of C₆H₆ in the above reaction. Explain your answer. (10 marks)

d. (i) "pKa value could be used as a measure of acidity in organic compounds". Explain this using aqueous ionization of acetic acid at 25°C as an example. (10 marks)

(ii) Give reason arrange the following carboxylic acids in an increasing order of pKa.

FCH₂CO₂H , ClCH₂CO₂H , CH₃CO₂H , CH₃CH₂COOH (15 marks)

2. a. (i) Derive an expression for the second order rate constant, $k_2 = \frac{1}{t} \frac{x}{a(a-x)}$, for the reaction



Where a = initial concentration of A
x = moles of A reacted after time t (20 marks)

(ii) How would you determine the second order rate constant by a graphical method? (20 marks)

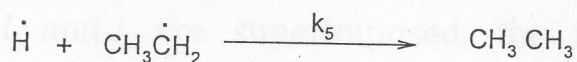
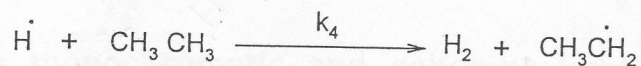
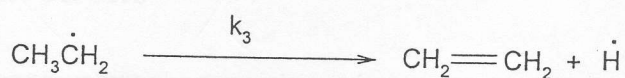
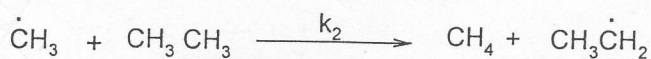
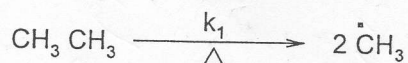
(iii) Show t_{1/2} of the second order reaction is inversely proportional to the initial concentration a (10 marks)

Turn over

b. Consider the following chain reaction



The reaction follows through the mechanism shown below.



(i) Identify the various steps involved in the above mechanism (15 marks)

(ii) What is meant by Steady State Approximation? (10 marks)

(iii) Derive an expression $\frac{d[\text{CH}_2=\text{CH}_2]}{dt} = \left(\frac{k_1 \cdot k_3 \cdot k_4}{k_5}\right)^{1/2} [\text{CH}_3\text{CH}_3]$

(25 marks)