



EASERN UNIVERSITY, SRI LANKA

FIRST EXAMINATION IN SCIENCE 2013/2014 (April/ May 2016)

SECOND SEMESTER

PH 104 ORGANIC REACTION MECHANISMS AND CHEMICAL KINETICS

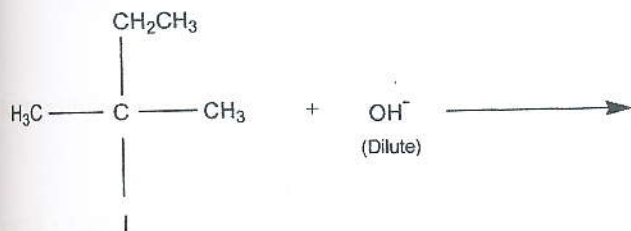
All questions

Time: One hour

- (a)
- Distinguish between a transition state and an intermediate state of an organic reaction
  - Explain the main features of  $S_N^1$  and  $S_N^2$  reactions.
  - In what way, the polar solvent is affecting the mode of nucleophilic substitution reactions.

(35 Marks)

- (b) Consider the following  $S_N^1$  solvolysis reaction



*tert*-pentyl iodide

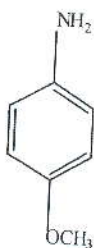
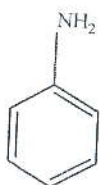
- Write the product and rate expression of the above reaction.
- What will happen on the reaction rate when doubling the concentration of *tert*-pentyl iodide and  $\text{OH}^-$ ?
- Suggest the mechanism for the above reaction

Contd.

(iv) Draw the fully labelled energy profile diagram. In the diagram, clearly indicate reactants, transition state(s), intermediate(s) and products.

(55 Marks)

(c) Arrange the following compounds in the increasing order of their basicity. Give a reason for your answers



(10 Marks)

2.

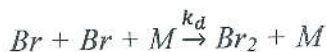
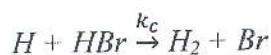
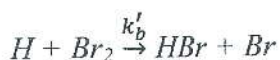
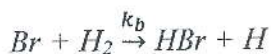
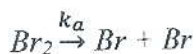
a) At  $500^{\circ}\text{C}$ , cyclopropane ( $\text{C}_3\text{H}_6$ ) rearranges to propene ( $\text{CH}_3\text{CHCH}_2$ ). The reaction is first order with a rate constant of  $6.7 \times 10^{-4} \text{ s}^{-1}$ .

- Calculate the molarity of cyclopropane after 25 minutes if the initial concentration is 0.25 M
- How many minutes does it take for the concentration of cyclopropane to drop from 0.150 M to 0.050 M at  $500^{\circ}\text{C}$ ?
- What is the half-life for the reaction at  $500^{\circ}\text{C}$ ?
- How long does it take for the concentration to drop to 25% of the original concentration at  $500^{\circ}\text{C}$ ?

(50 Marks)

Cont.

The mechanism of the reaction  $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$  is given by the following step reactions.



- i) Write the expressions for  $\frac{d[Br]}{dt}$  and  $\frac{d[H]}{dt}$
- ii) Determine  $[Br]$  and  $[H]$  by using steady state approximation
- iii) Show that the rate of formation of  $HBr$  is,

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]}$$

Where  $k = 2k_b \left(\frac{k_a}{k_b}\right)^{1/2}$  and  $k' = \frac{k_c}{k'_b}$

(50 Marks)

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