EASETRN UNIVERSITY, SRI LANKA

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

SENCOND SEMESTER

CH 104 ORGANIC REACTION MECHANISMS AND CHEMICAL KINETICS

wer all questions **Time: One hour**

1. (a)

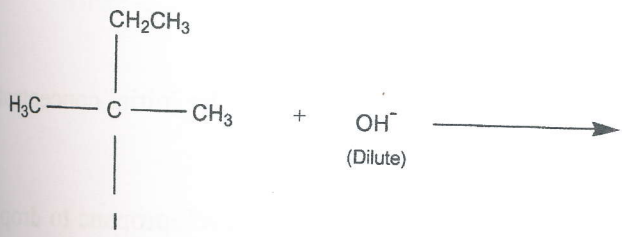
(i) Distinguish between a transition state and an intermediate state of an organic reaction

(ii) Explain the main features of S_N1 and S_N2 reactions.

(iii) In what way, the polar solvent is affecting the mode of nucleophilic substitution reactions.

(35 Marks)

(b) Consider the following S_N1 solvolysis reaction



tert-pentyl iodide

(i). Write the product and rate expression of the above reaction.

(ii). What will happen on the reaction rate when doubling the concentration of *tert*-pentyl iodide and OH^-?

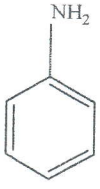
(iii). Suggest the mechanism for the above reaction

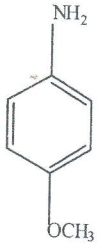
Contd.

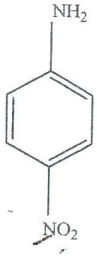
(iv) Draw the fully labelled energy profile diagram. In the diagram, clearly indicate the reactants, transition state(s), intermediate(s) and products.

(55 Marks)

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







(10 Marks)

2.

a) At 500°C, cyclopropane (C_3H_6) rearranges to propene (CH_3CHCH_2). The reaction is first-order with a rate constant of 6.7×10^{-4} s^{-1}.

i) Calculate the molarity of cyclopropane after 25 minutes if the initial concentration is 0.25 M

ii) How many minutes does it take for the concentration of cyclopropane to drop from 0.150 M to 0.050 M at 500 °C?

iii) What is the half-life for the reaction at 500 °C

iv) How long does it take for the concentration to drop to 25% of the original concentration at 500 °C?

(50 Marks)

Contd.

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

$$Br_2 \xrightarrow{k_a} Br + Br$$

$$Br + H_2 \xrightarrow{k_b} HBr + H$$

$$H + Br_2 \xrightarrow{k_b'} HBr + Br$$

$$H + HBr \xrightarrow{k_c} H_2 + Br$$

$$Br + Br + M \xrightarrow{k_d} Br_2 + M$$

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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