Eastern University, Sri Lanka

First Year Second Semester Examination in Science

2015/2016 (May/ June 2018)

CH104 Reaction Mechanism and Chemical Kinetics

(Proper)

Answer all questions **Time: One hour**

1. (a) Briefly *explain* why alcohols are less acidic than carboxylic acids.

(15 Marks)

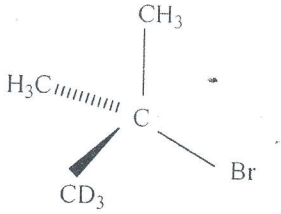
(b) (i) *Distinguish* between a transition state and an intermediate state of an organic reaction.

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

(iii) Explain how the polar solvent is affecting the mode of nucleophilic substitution reactions.

(35 marks)

(c) *Draw* The compound **P** is treated with an aqueous solution of sodium hydroxide and this reaction gave **Q** ($C_4H_7D_3O$) as the product. The rate of this reaction was found to depend **only** on the concentration of the compound **P**.



P

(i) *Draw* the structure (including the stereochemistry) of the product **Q**

(ii) *Write* down the mechanism involved in the formation of **Q** from **P**.

(iii) *Draw* a fully labelled energy profile diagram for the above reaction. Clearly indicate the reactants, transition state(s), intermediate(s) and products in the energy profile diagram.

(50 Marks)

2. (a) Derive the first order rate equation for the reaction

$$\boldsymbol{A + Other\ reactants \rightarrow Product}$$

The isomerization of methyl isonitrile to acetonitrile in the gas phase at 250° C

$$CH_3NC \rightarrow CH_3CN$$

is first order with a rate constant of $3 \times 10^{-3}\ s^{-1}$. If the initial concentration of CH_3NC is 0.107 M, how much time must pass for the concentration of CH_3NC to drop to 0.0142 M

(25 marks

(b) The isotope ^{32}P has a half-life of 14.3 days. If a sample contains 0.884 g of ^{32}P, what mass of ^{32}P will remain after 22 days? (Assume the radioactive decay of ^{32}P is the first order reaction)

(15 marks

(c) The mechanism of the reaction $CH_4(g) + Br_2(g) \rightarrow CH_3Br(g) + HBr(g)$ is given by the following step reactions.

$$Br_2 \xrightarrow{k_1} 2Br^*$$

$$CH_4 + Br^* \xrightarrow{k_2} CH_3^* + HBr$$

$$CH_3^* + Br_2 \xrightarrow{k_3} CH_3Br + Br^*$$

$$2Br^* \xrightarrow{k_4} Br_2$$

i) *Identify* the above steps weather initiation, propagation or termination.

ii) *Write* the expressions for $\frac{d[Br^*]}{dt}$ and $\frac{d[CH_3{}^*]}{dt}$

iii) *Determine* $[Br^*]$ and $[CH_3{}^*]$ using steady state approximation

iv) *Show that* the rate of formation of is CH_3Br ,

$$\frac{d[CH_3Br]}{dt} = k_2\sqrt{\frac{k_1}{k_4}}\,[CH_4][Br_2]^{1/2}$$

(60 marks