EASTERN UNIVERSITY, SRI LANKA

FIRST YEAR EXAMINATION IN SCIENCE

SECOND SEMESTER 2010-2011 (June/July 2013)

CH 104 CHEMICAL KINETICS AND ORGANIC REACTION MECHANISMS

(Proper &Repeat)

Answer all questions **Time: 01 hour**

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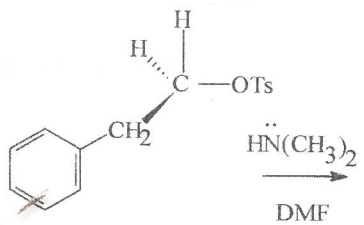
1) a) Explain main features of S_N1 and S_N2 reaction. [10 Pts.]

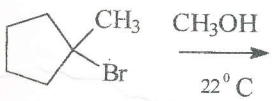
b) Predict the structure of the major organic products and indicate the predominant mechanism (S_N1 or S_N2) of the following reaction

i)



[10 Pts.]

ii)



[10 Pts.]

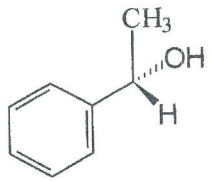
c) Write down the mechanisms of the reactions (i) and (ii) in part (b) [20 Pts.]

d) Draw the fully labeled graph of free energy vs. reaction coordinate for the reaction (i) in part (b) and clearly indicate the reactants, transition state(s) , intermediates (if exist) and products. [15 Pts.]

Turn over

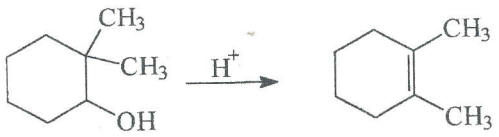
e) Explain by providing the mechanism why the reaction of compound 'X' with $SOCl_2$ proceed with intension of configuration and in the presence of pyridine it gives inversion of configuration

[20 Pts.]



X

f) Propose a detailed mechanism for the reaction shown below.



[15 Pts.]

2) (a) A reaction A⟶P has a second order rate law with rate constant $k = 3.50 \times 10^{-4}$ l mol s^{-1}.

i) Show that $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$, where $[A]$ = concentration of 'A' at time't' and $[A]_0$ = initial concentration of 'A'

[15 Pts.]

ii) Calculate the time required for the concentration of A changes from 0.26 mol l^{-1} to 0.11 mol l^{-1}

[20 Pts.]

iii) Calculate the half-life of the reaction

[15 Pts.]

Turn over

(b) The decomposition of ozone (O_3) in the gas – phase includes the species O_3, O_2 and M, where 'M' is an inert collision partner. The proposal mechanism is:

$$O_3 + M \rightleftharpoons O_2 + O + M$$

$$O + O_3 \rightarrow 2O_2$$

i) Identify the intermediate in the reaction [05 Pts.]

ii) Write down the expressions for $\frac{d[O]}{dt}$ and $-\frac{d[O_3]}{dt}$ [20 Pts.]

iii) Show that $[O] = \frac{k_1[O_3][M]}{k_2[O_2][M]+k_3[O_3]}$ and $-\frac{d[O_3]}{dt} = \frac{2k_1k_3[O_3]^2[M]}{k_2[O_2][M]+k_3[O_3]}$ [25 Pts.]

End of paper