

EASTERN UNIVERSITY, SRI LANKA
FIRST EXAMINATION IN SCIENCE 2005/2006 & 2006/2007
SECOND SEMESTER (March/April 2008)-PROPER
CH 104 CHEMICAL KINETICS AND ORGANIC REACTION MECHANISMS

Time allowed: **ONE Hour**

Answer all questions

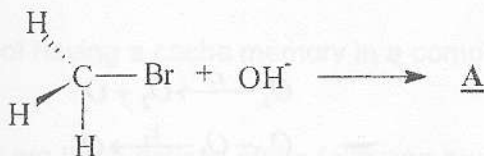
The use of a non-programmable calculator is permitted

1) a) Draw the resonance structures for the following compounds.



(30 marks)

b) Consider the following reaction obey $\text{S}_{\text{N}}2$ mechanism.



i) Give the structure (including the stereochemistry) of the product A.
(10 marks)

ii) Write down the mechanism of the above reaction.
(15 marks)

iii) On the basis of the mechanism, draw the fully labeled graph of free energy vs. reaction coordinate. In the graph, clearly indicate the reactants, transition state(s), intermediate(s) and products.
(20 marks)

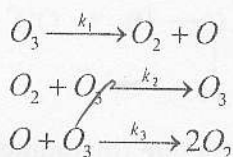
iv) Explain how the polar solvent affects the reactivity of $\text{S}_{\text{N}}2$ reaction.
(15 marks)

c) Briefly explain why alcohols are ^{less} more acidic than carboxylic acids.
(10 marks)

Cont.

- (2) (a) i) What is meant by a second order reaction ? (05 marks)
- ii) Show that the expression for the rate constant (k) of the following second order reaction $2A \rightarrow \text{Product}$ is $k = \frac{x}{ta(a-x)}$, where 'a' is the initial concentration of A and 'x' is the decrease in the concentration of A at time 't' (20 marks)
- iii) What is the unit of 'k'? (10 marks)
- iv) Show that the half - life period of a second order reaction is depend upon the initial concentration of the reactant. (15 marks)

(b) The mechanism of decomposition of Ozone, $2O_3(g) \rightarrow 3O_2(g)$, is given below



- i) Write down $\frac{d[O_3]}{dt}$ and $\frac{d[O]}{dt}$. (20 marks)
- ii) Determine $[O]$ by using steady state approximation. (15 marks)
- iii) Show that the rate law for the decomposition reaction is,

$$\frac{d[O_3]}{dt} = \frac{-2k k_3 [O_3]^2}{k_2 [O_2] + k_3 [O_3]} \quad (15 \text{ marks})$$

End