EASTERN UNIVERSITY, SRI LANKA
DEPARTMENT OF CHEMISTRY
FIRST YEAR SECOND SEMESTER EXTERNAL DEGREE EXAMINATION IN SCIENCE –2002/2003
(SEPT/OCT' 2005)
EXTCH 104 ORGANIC REACTION MECHANISM AND CHEMICAL KINETICS

Answer all questions **Time: 01 hour**

1)a. Define the rate law and order of a chemical reaction

b. Write an expression for the rate of the following elementary reactions using the rate law.

i. $Br^- + H^+ + H_2O_2 \longrightarrow HOBr + H_2O$

ii. $Cl^\circ + CH_4 \longrightarrow {}^\circ CH_3 + HCl$

iii. $O_3 + D^* \longrightarrow {}^*O_3 + D$

c. The decomposition of N_2O_5 in either gas phase or liquid phase proceeds via the following mechanism.

$$N_2O_5 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{K_2} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{K_3} 2NO_2$$

Steady state approximation can be applied to the two reactive intermediates NO_3 and NO.

(i) Define the term 'steady state approximation'.

(ii) Apply the steady state approximation for the intermediates NO_3 and NO.

(iii) Show that the above mechanism leads to first order kinetics if the steady state approximation is applied to the two reactive intermediates NO_3 and NO, and thus express the overall rate constant k in terms of K_1 , K_{-1} , K_2 and K_3.

2)a. For each of the following pairs of chemical species, indicate the one that is more stable. Give reason(s) for your answer.

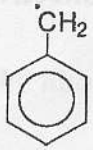
i . $(CH_3)_3C^+$ and $(CH_3)_2C^+H$

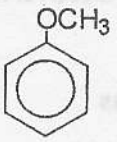
ii. $(CH_3)_2\bar{C}Cl$ and $(CH_3)_2\bar{C}Br$

Contd...

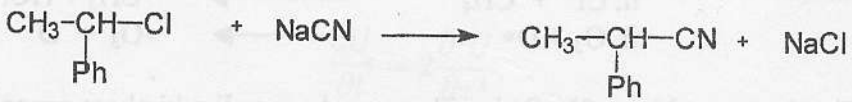
b. Explain why the rate of a S_N^1 reaction of tertiary alkyl halide with potassium hydroxide is faster than that of secondary alkyl halide and that in turn faster than that of primary alkyl halide.

c. Draw all the resonance structures for the following compounds

(I) 

(II) 

d. The following reaction follows S_N1 pathway



(i) Write down the equation for the expected rate of this reaction.

(ii) Write down the mechanism of the reaction indicating the slow and the fast steps and the stereochemistry of the product.

(iii) Draw the relevant energy profile diagram and write down the structure of the transition states and intermediate(s).

(iv) How will the rate of the reaction change if the concentration of NaCN is doubled.

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