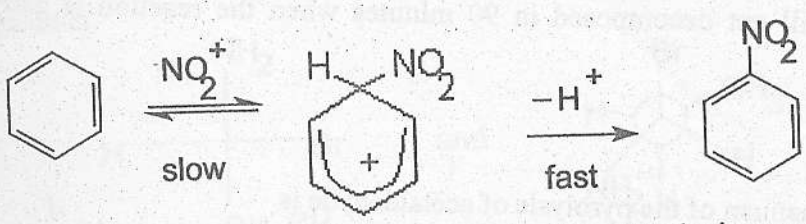
EASTERN UNIVERSITY SRI LANKA
FIRST EXAMINATION IN SCIENCE (2003/2004)
EXTERNAL DEGREE
SECOND SEMESTER (Oct./Nov. 2007)
EXTCH 104- CHEMICAL KINETICS AND ORGANIC REACTION MECHANISMS

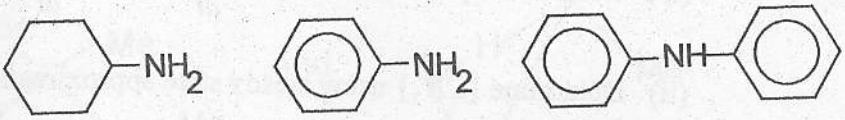
ANSWER ALL QUESTIONS **TIME – ONE HOUR**

1. (a) (i) What is meant by S_N^1 and S_N^2 reactions?
(ii) The nitration of benzene can be represented as follows:



(I) Write all possible resonance structures for the intermediate.
(II) Write rate expression for the above reaction.
(III) On the basis of the mechanism, draw and fully label the graph of free energy versus reaction co-ordinate for the above reaction.
(IV) On the same graph, draw the free energy profile for
(a) The nitration of toluene.
(b) The nitration of benzoic acid.

(b) (i) Arrange the following compounds in order by increasing basic strength.
(i) NH_3, CH_3NH_2, $(CH_3)_2NH$ and NH_2Cl

(ii) 

(ii) Consider the following reactions,

$$C_2H_5OCH_2CH_2Cl \xrightarrow[R_1]{H_2O} C_2H_5OCH_2CH_2OH$$

$$C_2H_5SCH_2CH_2Cl \xrightarrow[R_2]{H_2O} C_2H_5SCH_2CH_2OH$$

Rtes R_1 and R_2 of the above reactions were found to be in the order $R_1 << R_2$. Explain the above observation.

Contd.

2. (a) What is meant by 'first order reaction'?

(b) Derive an expression for rate constant of first order reaction.

(c) The reaction

$$SO_2Cl_2 \xrightarrow{K_1} SO_2 + Cl_2$$

is a first order reaction with $k_1 = 2.2 \times 10^{-5}$ sec^{-1} at 302 ^{0} C. What percentage of SO_2Cl_2 will get decomposed in 90 minutes when the reaction is carried out at 302 ^{0} C.

(d) The mechanism of the pyrolysis of acetaldehyde is

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO$$
$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$$
$$CH_3CO \xrightarrow{k_3} CO + CH_3CO$$
$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$$

(i) Write the expressions for $\frac{d[CH_3CHO]}{dt}$, $\frac{d[CH_3]}{dt}$ and $\frac{d[CH_3CO]}{dt}$ (30 marks)

(ii) Determine $[CH_3]$ using steady state approximation

(iii) Show that the rate of reaction of acetaldehyde is given by

$$\frac{d[CH_3CHO]}{dt} = -k_2(k_1/2k_4)^{1/2}[CH_3CHO]^{3/2},$$

where k_1 is very small compared to the other rate constants.

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