EASTERN UNIVERSITY, SRI LANKA
FIRST EXAMINATION IN SCIENCE – 2003/2004
SECOND SEMESTER
(June/July-2005)
CH104 ORGANIC REACTION MECHANISM AND CHEMICAL KINETICS

**Answer all questions**   **Time: 01 hour**

1) a(I) Distinguish between a transition state and an intermediate

(II) Compare S_N^1 and S_N^2 reaction mechanism with respect to
- i. Order
- ii. Number of steps
- iii. Rate and concentration of substrate and reactants
- iv. Stereochemistry
- v. Nucleophile
- vi. Rearrangements

(III) Explain why the rate of an S_N^1 reaction decreases as follows

3°halide fastest ⟶ 1° halide slowest
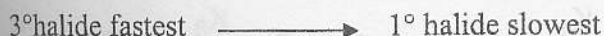
b. (I) Give two examples for strong and weak nucleophile respectively

(II) The nitration of benzene can be represented as follows,
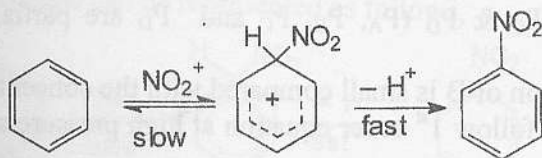
(i) On the basis of mechanism draw and fully label the graph of free energy VS reaction co-ordinate for above reaction. Label the position of reactants, transition state(s), intermediate and product(s)

(ii) Write a rate law for this reaction

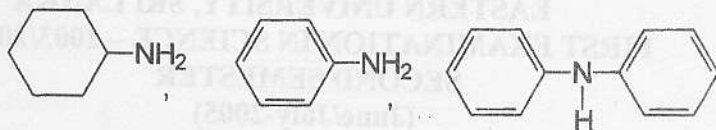(iii) On the same graph in (i) draw the free energy profile for
- a. The nitration of toluene
- b. The nitration of benzoic acid

c. Arrange the following compounds in order by increasing basic strength

(I) Ammonia , Methyl amine, Dimethyl amine, Chloroamine

(II)


2)a(i) What is meant by the term half-life of a reaction

(ii) A nuclear decomposition follows first order kinetics. A certain radioactive produ
of a nuclear reaction must be stored until it is 99.9% decomposed. If its half life
5000years, for how long it must be stored.

(iii) The thermal decomposition of N_2O_5 follows a first order kinetics. If the rate
constant at 25°C is 1.7×10^{-5} sec^{-1} at what rate does N_2O_5 decompose at this
temperature (Partial pressure is 50.0 KPa, Gas constant(R) = 8.314 $Jmol^{-1}K^{-1}$)

b(i). What is meant by the term steady state approximation in chemical kinetics.

(ii).

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B \qquad B + C \xrightarrow{K_3} D$$
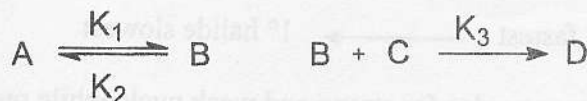
Determine the rate of expression for above reaction in terms of rate constants K_1, K_2
and the P_A, P_B, P_C & P_D (P_A, P_B, P_C and P_D are partial pressure of A,B,C and
respectively).

If the concentration of B is small compared with the concentration of A, C, D, show
this reaction may follow 1st order equation at high pressure and 2nd order equation at
pressure.

c. Explain the following observation

$$Me-\overset{\overset{O}{\|}}{C}-OH \qquad\qquad HOCH_2-\overset{\overset{O}{\|}}{C}-OH$$

pKa   4·7   3·83

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