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
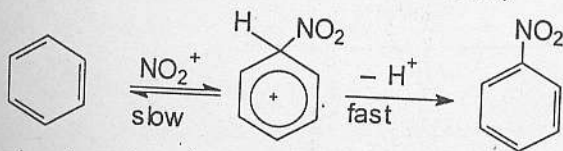   i. Order
   ii. Number of steps
   iii. Rate and concentration of substrate and reactants
   iv. Stereochemistry
   v. Nucleophile
   vi. Rearrangements

(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, product(s)

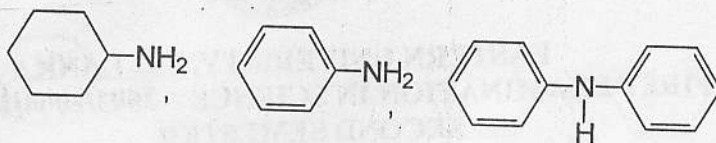(ii) Write a rate law for this reaction

(iii) On the same graph in (i) draw then 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)

$$\text{cyclohexyl-NH}_2 \qquad \text{phenyl-NH}_2 \qquad \text{phenyl-N(H)-phenyl}$$

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 produc of a nuclear reaction must be stored until it is 99.9% decomposed if its half life i 5000years, for how long it must be stored.

(iii) The thermal decomposition of N_2O_5 is 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).

$$A \underset{k_1}{\overset{}{\rightleftharpoons}} B \qquad\qquad B + C \xrightarrow{K_3} D$$
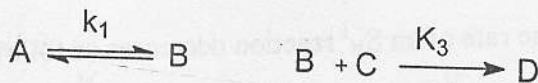
Determine the rate of expression for above reaction in terms of rate constants K_1, K_2 the P_A, P_B, P_C & P_D (P_A, P_B, P_C and P_D are partial pressure of A,B,C and D respectively If the concentration of B is small compared with the concentration of A, C, D, show th this reaction may follow 1st order equation at high pressure and 2nd order equation at lo pressure.

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