RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2017

FIRST YEAR [BATCH 2016-19]

Date : 18/05/2017 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm **Paper :** II [Gr-A] Full Marks : 40

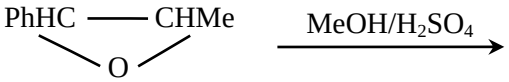
[Use one Answer Book for Unit I and another Answer Book for Unit II & III]

(Attempt one question from each Unit)

Unit I

[15 marks]

1. a) Indicate with plausible mechanism what will happen in the following reaction : [2]

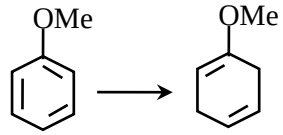


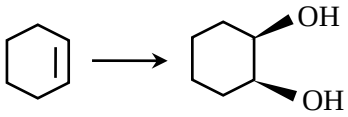
b) Explain the stereochemistry of the product with suitable mechanism when *threo* isomer of PhCH(Me)CH(Me)OTs is treated with acetic acid in presence of sodium acetate. [2]

c) Between NaCl and NaBr in DMSO solution, $Cl^{(-)}$ behaves as a better nucleophile than $Br^{(-)}$. Explain. [1]

d) Write down the following conversions with proper mechanism.

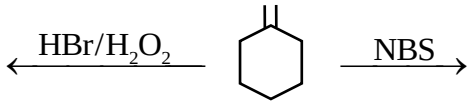
i) 

ii) 

iii) 

(using Woodward's reaction) [3×2]

e) Write down the structures of the major products in the following reactions with explanation. [2]



f) Predict the major product when 2-bromo-3-methylbutane reacts with KOEt/EtOH. [2]

2. a) $I^{(-)}$ ion is a good nucleophile as well as a good leaving group. Explain why. How can you use this dual property of the ion to catalyse the following reaction? [2·5]

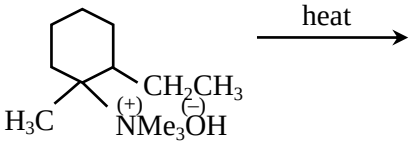
$$MeBr + H_2O \rightarrow MeOH + HBr$$

b) What happens when $F_3C - CHCl_2$ is heated with EtONa in ethanol? By which path the reaction occurs? [1·5]

c) β -Thioethoxyethyl chloride hydrolyses 10^4 times more rapidly than β -ethoxyethyl chloride under comparable conditions. Provide an explanation to this marked rate difference. [2]

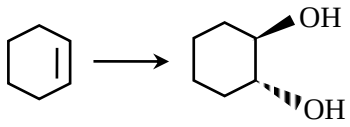
d) How can you convert (R)-2-pentanol to (S)-2-pentanol? [2]

e) Give the structures of all possible alkenes that could be formed in the following reaction. Indicate the major product and explain its formation. [3]



f) How can you convert *cis*-2-butene to *trans*-2-butene? [2]

g) Write down the following conversion with proper mechanism : [2]



(using *m*cpba)

Unit II [13 marks]

3. a) Show that $ds = n\bar{C}_p\, d\,InV + n\bar{C}_v\, d\,In\,P$ for an ideal gas. [3]

b) How much heat (in Joules) is rejected to the surroundings when 10g of water at 0^oC freezes to ice at 0^oC, in a Carnot refrigerator working between 298K and 268K. [3]

c) Given that $C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$, along with this also use the expression for combined first and 2nd law to prove $C_p - C_v = \alpha^2 VT/\beta$. [3]

b) Draw the typical T–P diagram as obtained in a J–T experiment for a real gas. Explain which region in the T–P space you expect the gas to cool down during the experiment. [2+2]

4. a) A certain ideal gas has $\bar{C}_v = a + bT$, where a = 25 J mol^{-1} K^{-1} and b = 0.03 J mol^{-1} K^{-2}. If 4 moles of this gas go from 300K and 2 atm to 500K and 3 atm, calculate ΔH and ΔS for the process. [3]

b) If $A(\text{Helmholtz free energy}) = f(T) - RT(\bar{V} - b) - \frac{a}{\bar{V}}$, find out the expression of pressure. [2]

c) Derive the expression for the entropy of mixing for two ideal gases and find out the condition for the maximum value of ΔS_{mix}. [2+1]

d) If $\left(\frac{\partial H}{\partial P}\right)_T = 0$ for a gas, then integrating the proper thermodynamic equation of state. Show that *V* is proportional to *T*. [2]

e) Starting with clausius inequality, show that at constant *T* and *P* for any spontaneous process $\Delta G < 0$. [3]

Unit III [12 marks]

5. a) 'The reaction having order greater or equal to one does not go to completion at finite time' – Justify. [2]

b) For the reaction $A \underset{R_2}{\overset{R_1}{\rightleftharpoons}} B$, if $R_1 = 3R_2$, plot the concentrations of *A* and *B* as a function of time in a same graph and indicate the equilibrium concentration of *A* and *B*. [3]

c) At 200^oC, the gas phase reaction $A \rightarrow 2B + C$, (*A*, *B*, *C* are ideal gases) is observed to be second order. Starting with pure *A*, it was found that at the end of 10 minutes the total pressure is 176mm of Hg and after a long time 270mm of Hg. Calculate the value of rate constant. [3]

d) Using collision theory, estimate the collision number for 1 mole of HI present in a volume of $1m^3$ at 300K. Take d_{HI} = 0·35nm. If the activation energy for HI decomposition is 184 KJ $mole^{-1}$, what rate constant does kinetic theory predict at 300°C? [2+2]

6. a) In a reaction, the effective rate constant $k' = 2\left(\frac{k_2}{k_3}\right)\left(\frac{k_1}{k_5}\right)^{1/2}$ at the early stage of reaction. Calculate the effective activation energy of the reaction. [2]

b) Using Lindemann mechanism show that the rate of an unimolecular reaction would be half of the maximum rate when rate of deactivation is same as rate of product formation. [3]

c) The rate constant of a chemical reaction is given by $k = aT^m e^{-\frac{E'}{RT}}$, where a, m and E' are the temperature Independent constants. Show that Arrhenius preexponental factor, $A = aT^m e^m$. [2]

d) Urease is a typical enzyme causing decomposition of urea, which follows the following mechanism, $E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} P + E$

i) Show that when $[s]_0$ is equal to K_M and [P] is negligible then $\frac{[ES]}{[E]_0} = 0{\cdot}5$. [2]

ii) Draw the Lineweaves Burk plot for enyme kinetics and show how the linear plot is helpful for the determination K_M. [3]

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