RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

B.A./B.SC. THIRD SEMESTER EXAMINATION, DECEMBER 2013

SECOND YEAR

Date : 14/12/2013 **CHEMISTRY (Honours)**

Time : 11 am – 1 pm Paper : III Full Marks : 50

[Use Separate Answer Scripts for each group]

Group – A

(*Answer **one** question from each unit*)

Unit – I

1. a) Starting from the expression of van't Hoff's reaction isotherm for a reaction in gas phase, derive van't Hoff's equation. [3]

b) Consider the dissociation reaction $N_2O_4(g) = 2NO_2(g)$. Show that, at equilibrium, the fraction of $N_2O_4(g)$ dissociated at a pressure P is given by, $\alpha = \sqrt{\dfrac{K_p}{K_P + P}}$ [3]

c) Derive $\left[\dfrac{\partial E_{eq}}{\partial T}\right]_P$ and hence comment on how does the expression corroborate the La Chatelier's principle. [3+1]

d) Derive the expression of the chemical potential in terms of enthalpy function. Can it be termed also as the partial molar enthalpy. [3]

2. a) Determine the effect of introduction of an inert gas, at constant temperature and pressure, on the position of equilibrium of the reaction : $N_2(g) + 3H_2(g) = 2NH_3(g)$ [3]

b) Consider the equilibrium : $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

At 1000K and 1 atm, $C_2H_6(g)$ is introduced into the vessel, where the reaction takes place. At equilibrium, the reaction mixture is found to contain 26 mol percent of $C_2H_4(g)$. Find out the equilibrium pressure of the reaction mixture and K_P at 1000K. [3]

c) Draw Gibbs energy (G) of a reacting system against degree of advancement (ε) of the reaction. Comment on the slopes of the curve at $\varepsilon < \varepsilon_e$, $\varepsilon = \varepsilon_e$ and $\varepsilon > \varepsilon_e$ where ε is the value of degree of advancement at equilibrium. [4]

d) Show how K_P, K_C and K_X are dependent on pressure? [3]

Unit – II

3. a) Consider the parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, where k_1 and k_2 are the respective specific rates. The activation energies of these reactions are E_1 and E_2. Show that the overall activation energy E is given by $E = \dfrac{k_1E_1 + k_2E_2}{k_1 + k_2}$. [2]

b) At 100°C, the gaseous reaction $A \rightarrow 2B + C$ is observed to be first order. On starting with pure A, it is found that at the end of 10 minutes, the total pressure of the system is 176·0 mm Hg and after a very long time it is 270·0 mm Hg. Find the half decomposition time of the reaction. [3]

c) Consider the following consecutive 1st order reactions and derive the expression for t_{max}, i.e. when [B] is a maximum in terms of k_1 and k_2 : $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ Assume at t = 0, $[B] = [C] = 0$ and [B] at any instant $= \dfrac{k_1[A]_0}{k_2 - k_1}\left(e^{-k_1t} - e^{-k_2t}\right)$. Draw concentration versus time plots for A, B and C assuming, $k_2 \gg k_1$. [3+1]

d) Show that for an elementary reaction $A+B \rightarrow C+D$, the expression of the rate constant obtained from collision theory is given by, $k = N_0 \pi \sigma_{AB}^2 \left(\sqrt{\frac{8k_BT}{\pi\mu}} \right) e^{-\frac{E_a}{RT}}$, where N_0 is the Avogadro number and E_a is the activation energy, the other terms having their usual meanings. [3]

4. a) Consider the following Lindemann mechanism for the unimolecular decomposition of a molecule A in the presence of a species M (which may be any molecule) :

$$A+M \xrightarrow{k_1} A^* + M;\ A^* + M \xrightarrow{k_{-1}} A+M;\ A^* \xrightarrow{k_2} \text{product}\,(P)$$

Using the Steady-state approximation method derive the rate law for the formation of the product (P).

Is the Lindemann mechanism applicable to solutions? [3+1]

b) With the help of Michaelis-Mention equation, how would you ascertain the value of V_{max} and k_m using the Lineweaver Burk method. [2]

c) For the reaction of hydrogen with iodine, the rate constant is $2{\cdot}45 \times 10^{-4}$ L/mols at 302°C and 0·950 L/mols at 508°C.

Calculate the activation energy and the frequency factor for this reaction. What is the value of the rate constant at 400°C? [4]

d) Can the activation energy of a (simple) reaction be zero or negative?

[$Ea/_{RT}$ may be taken to be much less than 1] [2]

Group – B

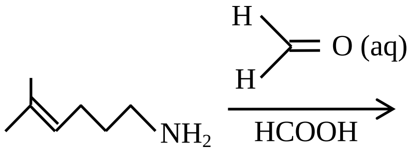
(*Answer* **one** *question from each unit*)

Unit – I

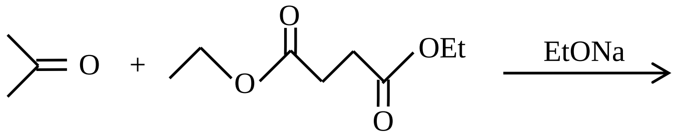
5. a) What is the major product when allene is subjected to acid catalysed hydration? Give explanation.

b) Predict the product of the following reactions, with mechanism :

i)

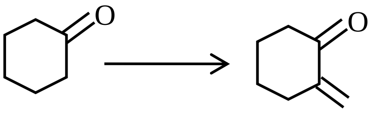


ii)



c) Carry out the following conversions (mechanism not required)

i)



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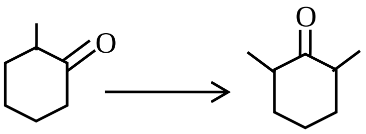
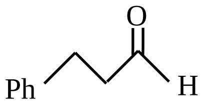
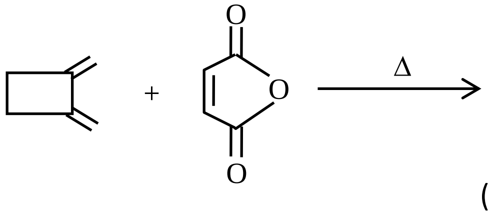


iii) $PhCH_2C \equiv CH \rightarrow$

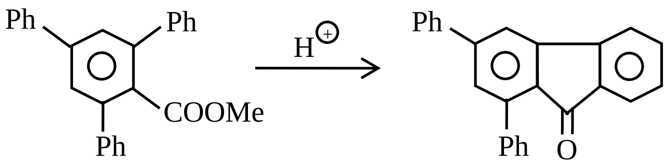


d) How would you convert acetone to n-propane without using acid or alkali. [1½+(2½×2)+(2×3)+2½]

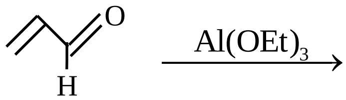
6. a) Predict the product of the following reaction and give explanation by FMO approach :



b) Give mechanism of the following transformation—

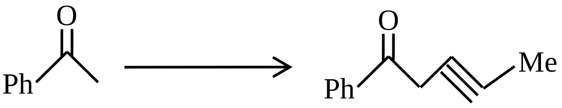


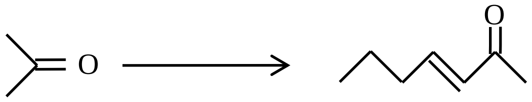
c) Predict the product of the given reaction with mechanism—



d) Chloral forms a stable hydrate while trimethylacetaldehyde does not — provide an explanation.

e) Carry out the transformations (mechanism not required) —

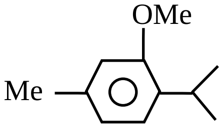
i) 

ii) 

f) $R_2CHCOOEt$ does not undergo Claisen ester condensation in presence of base NaOEt in EtOH — why? How would you accomplish the condensation of the same substrare? [3+2+2+2+(2×2)+2]

Unit – II

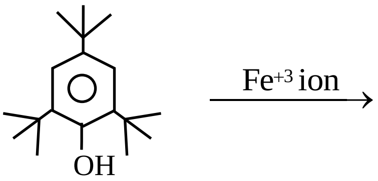
7. a) Compound (I) on treatment with mixed acid forms only one aromatic product of which the molecular formula is $C_8H_8N_2O_5$. Account for the reaction.

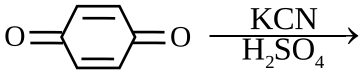


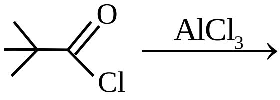
(I)

b) Phenol can not be nitrated with conc. HNO_3 / conc. H_2SO_4 acid mixture to get p-nitrophenol — Why? How would you convert phenol to p-nitrophenol? Give mechanism of your method.

c) Predict the product(s) of the following reactions. Give mechanism in each case.

i) 

ii) 

iii) Benzene + 

[2+2+(2×3)]

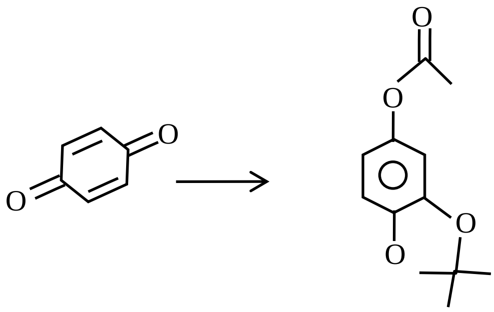
8. a) Using chloromethylation reaction, convert benzene into benzyl chloride. Give mechanism.

b) Both ortho and meta bromoanisole give the same product on treatment with sodamide in liquid ammonia. Write the product with explanation.

c) What happens when p-cresol is treated with chloroform and aqueous alkali? Give explanation for you answer.

d) Carry out following conversions (mechanism not required) :

i)



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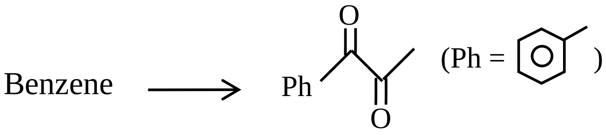

[2+2+2+(2×2)]

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