UG/I/CHEM/H/I/17

2017

CHEMISTRY

[Honours]

PAPER – I

Full Marks : 90

Time : 4 hours

The figures in the right hand margin indicate marks

Use separate answer scripts for Group A and B

GROUP – A

(*Organic*)

Subgroup – A(a)

Answer any **one** question : 15 × 1

1. (*a*) (*i*) Compare the $C_2 - C_3$ bond distances in propene and propane-give justification.

(*ii*) Explain the term 'steric inhibition of resonance' with an example.

(*iii*) Draw π MO's of allyl radical and mention the orbitals which can act as HOMO and LUMO.

(*iv*) How can you separate *o* and *p* isomers of hydroxy-benzaldehyde. $1\frac{1}{2} \times 4$

(*b*) How many stereomers are possible with the structure

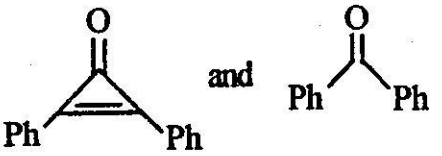
$HO_2C - CHOH - CHOH - CHOH - COOH$

Draw one *meso*-isomer and designate the centre which is 'reflection invariant'. 1 + 1 + 1

(*c*) What are the similarities and dissimilarities between 'Conjugation' and 'hyperconjugation'? 2

(*d*) 'Hydride ion' from a chiral source is allowed to attack on Re-face of acetophenone. Write the configuration of the product. 2

(*e*) Compare the dipole moment of



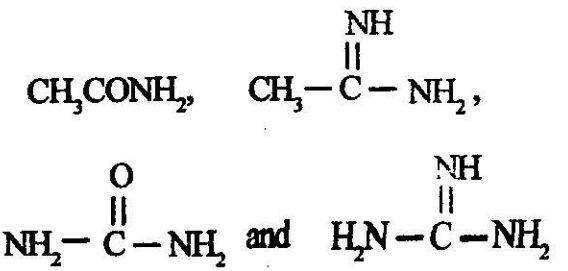
2

2. (*a*) (*i*) Compare the acidity of CH_3COOH and CF_3COOH considering entropy factors operating during their ionisation in water.

(*ii*) Arrange the following compounds in their increasing order of acidities with proper reasoning.

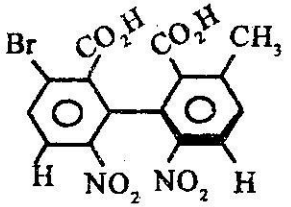
$PhCO_2H$, o, m and p isomers of hydroxy bensonic acid

(*iii*) Arrange the following compounds in their decreasing order of basicities and give reason.



2 × 3

(*b*) (*i*) Predict R|s configuration of



(*ii*) Draw the structure of syn-benzaldoxime. $1\frac{1}{2}+1$

(*c*) Find out the symmetry elements present in the following compounds : $1\frac{1}{2}\times 2$

$CHCl_3$ and $H_2C=C=CH_2$

(*d*) The observed rotation of a 10% aqueous solution of glucose is x° when kept in a cell of path length 5 cm. Calculate the specific rotation of glucose. $1\frac{1}{2}$

(*e*) Write schematically the process of resolution of ± 2-octanol. 2

Subgroup – A(b)

Answer any two questions : 10×2

3. (*a*) **How can you determine a reaction to be**

inter-or intra-molecular ? Explain with a suitable crossover experiment. $2\frac{1}{2}$

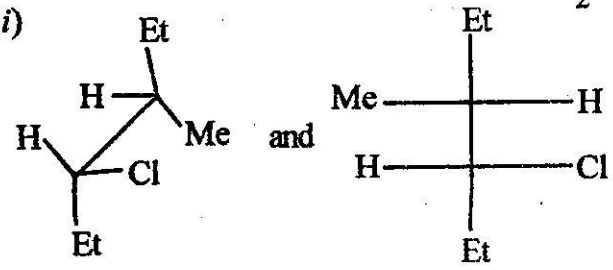
(*b*) Draw the preferred conformation of 1, 3,-ditertiary butyl cyclohexane and justify your drawing. $1\frac{1}{2}$

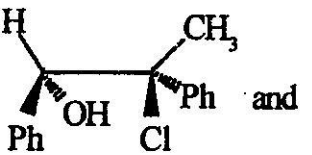
(*c*) Draw Newman projection formula of 2R, 3S-2, 3-dimethoxy-butane and designate it by D/L-nomenclature. $1\frac{1}{2} \times 1$

(*d*) 5-chloro-2hexyl tosylate is solvolysed in acetic acid with little participation by chlorine but solvolysis in trifluoroacetic acid participation by chlorine becomes the major reaction – Explain showing the mechanism of the reaction. $3\frac{1}{2}$

4. (*a*) Assign the following pair of compounds as homomer, enantiomer or diastereomer. $1\frac{1}{2} \times 2$

(*i*)



(*ii*) 

(*b*) Draw the energy profile diagram of an exothermic reaction shown below schematically.

$$\text{Reactant} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \text{Intermediate} \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} \text{Product}$$

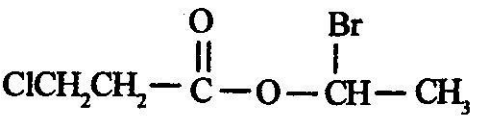
Given $k_{-1} > k_1 > k_2 > k_{-2}$.

Which one is the r.d.s in the forward direction. 3

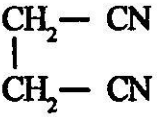
(*c*) In gaseous phase F^-, OH^- and NH_2^- are equally reactive towards CH_3Cl although their intrinsic nucleophilicities are not same – explain. 2

(*d*) Write IUPAC nomenclature of

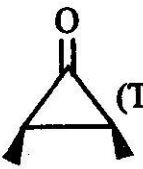
(*i*)

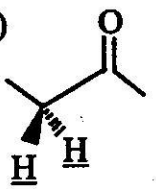


2

(*ii*) 

5. (*a*) Assign the topic reactionship between the indicated atoms, groups or faces in the following molecules : 2

(*i*)  (Two faces of the carbonyl group)

(*ii*)  (Underlined H-atoms)

(*b*) Compare the following with proper explanation : 3×2

(*i*) Rotational energy barriers across C – O and C – N bonds of $CH_3 - OH$ and $CH_3 - NH_2$.

(*ii*) Enol contents of $CH_3COCH_2COCH_3$ and $CH_3COCH(CH_3)COCH_3$

(*iii*) Boiling points of n-hexane and cyclohexane.

(*c*) CrO_3-oxidation of R_2CHOH is faster than R_2COOH – Explain. 2

6. Explain the following : $2\frac{1}{2} \times 4$

(*a*) During hydrolysis reaction diarylmethyl halide initially reacts faster but gradually rate decreases unlike tertiary butyl chloride where no decrease in rate was observed.

(*b*) *Cis*-1, 2-Dimethylcyclohexane is optically inactive although it is chiral in chair-form.

(*c*) Cyclopropylmethyl halide is more reactive than benzyl halide.

(*d*) Solvolysis of L-*threo*-3-phenyl-2-butyl tosylate in acetic acid produces 96% of *threo* acetate with approximately equal amounts of D-and L-isomers.

Subgroup – A(c)

7. Answer any *five* questions from the following : 2×5

(*a*) Which one of the following carbenes reacts faster with $CH_2 = CH - CO - CH_3$ and why?

(*i*) : CH_2

(*ii*) : $C(NMe_2)_2$

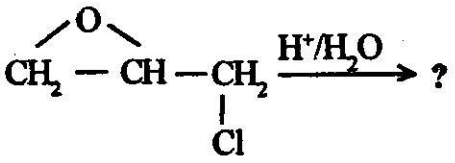
(*b*) $\dot{C}H_3$ and $\dot{C}l$ react differently to generate radical from $CH_3 - CH_2 - CH_2 - COOH$ – Explain showing the radicals formed in two cases.

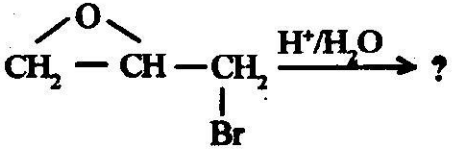
(*c*) Compare the acidity of the diastereomers of 4-tert. butyl-cyclohexane carboxylic acid.

(*d*) Write the product when $R_2C = CH - CH_2OH$ is treated with $SOCl_2$. Explain the reaction with mechanism.

(*e*) Predict the products in the following

reactions showing mechanism of the reactions :

(*i*) 

(*ii*) 

(*f*) $NR^1R^2R^3$ is not resolvable but $PR^1R^2R^3$ is resolvable – explain.

(*g*) Compare the relative population of gauche conformation of the following compounds :

n-butane, 1, 2-dichloroethane and ethane-1, 2-diol.

(*h*) Write down the differences between 'dihedral angle' and 'tortional angle'.

(*i*) "All prochiral centres are prostereogenic but reverse is not true" - Justify with example.

GROUP – B

(*Inorganic*)

Subgroup – B(a)

Answer any **one** question : 15×1

8. (*a*) State Heisenberg's uncertainty principle and explain it's significance. 2

(*b*) How will you account for the extrastability of d^5 subshell ? 3

(*c*) Show how electronegativity varies with hybridisation and bond order. 4

(*d*) $MgCO_3$ is thermally less stable than $CaCO_3$. – Explain. 2

(*e*) Why liquid ammonia is called water like solvent ? Complete the following reactions in liquid ammonia : 4

(*i*) $NH_4I + PbNH \longrightarrow$

(*ii*) $CO(NH_2)_2 + NH_3 \longrightarrow$

9. (*a*) The I – F bond energies in IF5 and IF_7 molecules are 278 and 231 KJ/mole respectively. Compare the Pauling electronegativity of Iodine in each of these molecules [Givem : Electronegativity of fluorine is 3·98 ; I – I and F – F bond energies 149 and 155 kJ/mole respectively. 4

(*b*) What is the difference between equivalent and non equivalent hybrid orbitals ? Explain with examples. 3

(*c*) Compare the radial distribution plots for 2s and 2p orbitals and comment on their relative penetrating property. 3

(*d*) Indicate with reasons, the direction of the following reactions : 3

(*i*) $BF_3H^- + BH_3F^- \rightleftharpoons BF_4^- + BH_4^-$

(*ii*) $HgS + 2HCl \rightleftharpoons HgCl_2 + H_2S$

(*e*) Explain why solubility of HgX_2(X = Cl, Br, and I) decreases from chloride to iodide. 2

Subgroup – B(b)

Answer any **two** questions : 10×2

10. (*a*) The atomic radii of Z_r and H_f are almost indentical. Explain. 2

(*b*) Show that the Bohr's postulate of quantized angular momentum for an electron moving in a circular orbit can be derived by de Broglie's principle. 3

(*c*) Explain why $Al(CH_3)_3$ is readily hydrolysed whether $B(CH_3)_3$ is unaffected by water at room temperature. 2

(*d*) Lithium is the only alkali metal to form stable nitride. – Explain. 2

(*e*) What is buffer capacity of a buffer. 1

11. (*a*) Using Pauling's method, calculate the ionic radii of Na^+ and F^- ions in NaF crystal. [Given : $d_{Na^+ - F^-} = 231$ pm] 3

(*b*) Explain the following reaction in the light of acid-base concept.

$$6CaO + P_4O_{10} = 2Ca_3(PO_4)_2$$ 2

(*c*) Predict the geometry of BrF_4^+ and BrF_4^- ions using VSEPR theory mentioning the nature of hybridisation. $1\frac{1}{2} + 1\frac{1}{2}$

(*d*) $LiAlH_4$ explodes violently with water while $NaBH_4$ does not. 2

12. (*a*) What is basic berilyum acetate ? Discuss it's structure. 3

(*b*) Why does the bond angle ∠O-N-O decreases in the following order : 3

$$NO_2^+ > NO_2 > NO_2^-$$

(*c*) Explain why $LiClO_4$ is much more soluble than $CsClO_4$ in water. 2

(*d*) Determine the ground state term symbol for the ion Co^{2+}. 2

13. (*a*) What optical transition in He^+ spectrum

would have the same wave length as the first Lyman transition of Hydrogen atom (Neglect the effect of reduced Mass.) 3

(*b*) Au shows the heighest electron affinity among all the metals – Explain. 2

(*c*) Choose and explain : $1\frac{1}{2}+1\frac{1}{2}$

(*i*) Strongest protonic acid :

$HClO, HClO_2, HClO_3, HCLO_4$

(*ii*) Strongest Lewis acid

BF_3, BCL_3, BBr_3, BI_3.

(*d*) Solution of Na in liquid NH_3 is paramagnetic; the magnetic susceptibility decreases with increase in metal concentration. Explain. 2

Subgroup –B(c)

14. Answer any *five* questions : 2×5

(*a*) Calculate the effectine nuclear charge for a 3d electron of chromium ($z = 24$).

(*b*) The electronegativity of Ga is heigher than that of Al. Explain.

(*c*) The solubility of CaF_2 in water At 18°C is $2{\cdot}04 \times 10^{-4}$ moles $litre^{-1}$. What is the solubility product of CaF_2 ?

(*d*) Derive out the relation between kinetic energy of a particle and wavelength associated with it's wave.

(*e*) Compare the solubility of $MgSO_4$ and $BaSO_4$ in water.

(*f*) Na^+ and Ag^+ ions have similar ionic radii. Which aqua ion is the stronger acid and why ?

(*g*) Sb_2O_3 is white while Sb_2S_3 is orange yellow. – Explain.

(*h*) What is the difference between Bohr-H atom and wave mechanical H-atom ?

(*i*) Apply Bent's rule to explain the structure of SF_4.

(*j*) Zn is found in nature both as ZnO and ZnS but Hg is obtained only as HgS. – Explain.
