UG/I/CHEM/H/I/18

2018

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 Group–B

GROUP – A

(*Organic*)

Subgroup-A(a)

Answer any **one** question : 15×1

1. (*a*) (*i*) Calculate the double bond equivalent of C_3H_7N and $C_7H_6O_2$.

(*ii*) Draw the canonical forms of the following compounds and indicate the major contributor :

$CH_3-\overset{\oplus}{C}H-O-C_2H_5$ and $\overset{\ominus}{C}H_2-CH=CH-\overset{O}{\overset{\|}{C}}-CH_3$

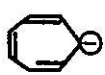
(*iii*) Indicate the symmetry elements present in *cis*-2-butene and *trans*-2-butene.

(*iv*) Draw the orbital picture of the following compound indicating the hybridization state of the key atoms : $1\frac{1}{2} \times 4$

$CH_3-CH=C=O$

(*b*) Which of the following compounds are aromatic, anti-aromatic or non-aromatic ? Justify. 2

(*i*) 

(*ii*) 

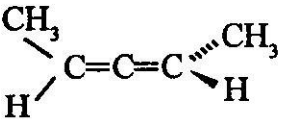
(*iii*) 

(*iv*) 

(*c*) Compare dipole moments between 2

CH_3CH_2Cl and $CH_2=CH-Cl$

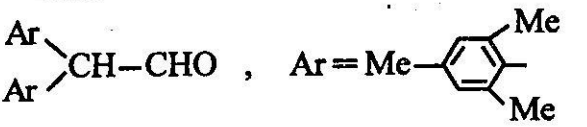
(*d*) Predict R/S configuration of the following compound and state whether it is asymmetric or disymmetric ? 3



(*e*) What is primary kinetic isotope effect (PKIE) ? Give an example. 2

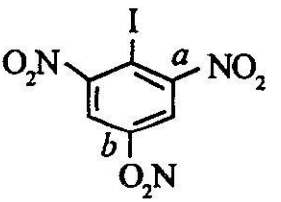
2. (*a*) (*i*) Draw the π-M.O. diagram of 1,3,5 -hexatriene and indicate the HOMO and LUMO at excited state. 3

(*ii*) Draw the enol tautomer of the following compound and indicate the most stable form with reasons : 2



(*iii*) Explain enantiotopic and diastereotopic faces and ligands with examples. 2

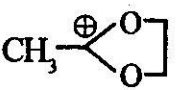
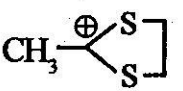
(*b*) Which C-N bond (*a* or *b*) has higher bond length and why ? 1 + 1

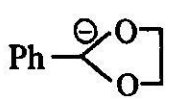
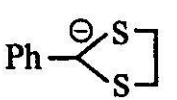


(*c*) Compare the basicities of the following compounds with proper explanations : 2

Bu_3N, Bu_2NH and $BuNH_2$ in CCl_4 solution.

(*d*) Compare the stabilities of each pair in the following with reasons.

(*i*)  and 

(*ii*)  and  $1\frac{1}{2}+1\frac{1}{2}$

(*e*) Why neo-pentyl bromide can not undergo S_N2 displacement ? Explain. 1

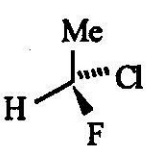
Subgroup-A(b)

Answer any **two** questions : 10×2

3. (*a*) Draw orbital picture of carbene in sp^2 -singlet, sp^2-triplet and sp-triplet states. Why dimethoxycarbene fails to add to an alkene ? 2+1

(*b*) Draw the energy profile diagram of 1, 2-dichloroethane for C—C bond rotation. Compare the relative stability of the conformations with explanation. 2+1

(*c*) Assign the following pair of compounds as homomer, enantiomer or diastereomer : 1 + 1

(*i*) 

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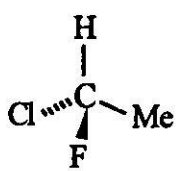
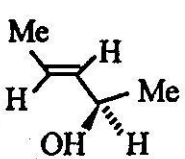


(*ii*) 

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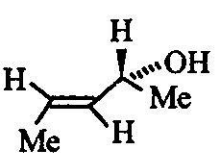


(*d*) Draw the preferred conformation of 1-methyl-1-phenyl cyclohexane with proper explanation. 1 + 1

4. (*a*) Write IUPAC names of $\frac{1}{2} \times 4$

(*i*) HO_2C-CO_2H

(*ii*) $(CH_3)_2CHCONH_2$

(*iii*) $CH_3-O-CH(CH_3)_3$

(*iv*) $CH-\underset{\underset{Cl}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

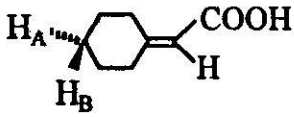
(*b*) Which mechanism S_N1 and S_N2, is favourable for reactions with each of the following substrates. Explain. 3

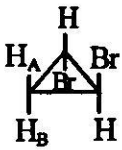
MeO–C$_6$H$_4$–CH_2–Cl ; O_2N–C$_6$H$_4$–CH_2Cl,

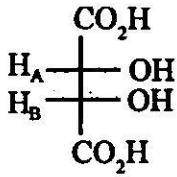
$MeO-CH_2-Cl$

(*c*) $Cl^{\ominus}$ ion of $Bu_4N^{\oplus}Cl^{\ominus}$ in acetone is a better nucleophile than that of LiCl in the same solvent. Explain. 2

(*d*) Identify H_A and H_B in each of the following structures as homotopic, enantiotopic or diastereotopic and explain. 1 + 1 + 1

(*i*) 

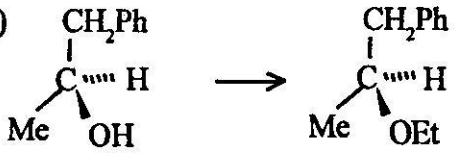
(*ii*) 

(*iii*) 

5. (*a*) When $PhCH_2Br$ is added to a suspension of KF in C_6H_6 no reaction occurs. However when a catalytic amount of 18-crown-6 ether is added, $PhCH_2F$ can be isolated in high yields. Explain the above observation. 2

(*b*) Carry out the following transformations : $1\frac{1}{2} + 1\frac{1}{2}$

(*i*) 

(*ii*) 

(*c*) What are the necessary structural features for a biphenyl compound to be dissymetric ? Explain with a suitable example. 2

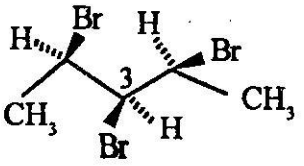
(*d*) Draw the preferred conformation of the following compounds : 1+1+1

(*i*) Trans-1, 3-di-tert-butylcyclohexane

(*ii*) cis-cyclohexane-1, 3-diol

(*iii*) 1, 2-difluoroethane.

6. (*a*) Comment on the stereogenecity and chirotopicity of C-3 of the following compound : 2

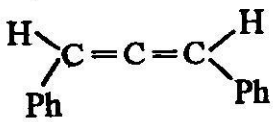


(*b*) Explain why (S)-3-phenylbutanone loses optical activity in alkali medium. 2

(*c*) Why $EtSCH_2CH_2Cl$ reacts with ethanol at a rate many fold faster than $EtOCH_2CH_2Cl$ under similar conditions ? Explain. 2

(*d*) (*i*) Comment on optical activity of trans-1, 2-dimethyl-cyclohexane.

(*ii*) Explain whether the following compounds are resolvable or not : 2 + 2



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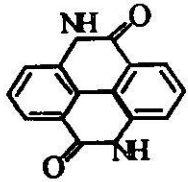
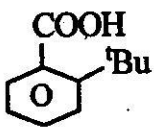


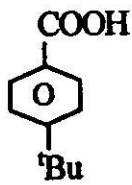
Subgroup-A(c)

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

(*a*) Compare acidities of the following two compounds with reason :



and



(*b*) What is sacrificial hyperconjugation ? Give example.

(*c*) Justify whether biphenyl is aromatic or not.

(*d*) Arrage the following in order of basicity with reasons :

$$\overset{\ominus}{O}H, \quad \overset{\ominus}{O}C_2H_5, \quad (CH_3)_3C\overset{\ominus}{O}, \quad CH_3COO^{\ominus}$$

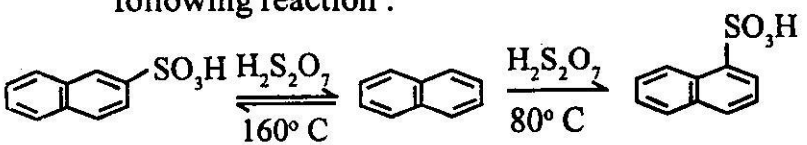
(*e*) Give the product with stereochemistry when hydride ion attacks the Si-face of 2-butanone.

(*f*) Write schematically the process of resolution of (±)-2-ethylhexanoic acid.

(*g*) What is pseudorotation ? Give an example.

(*h*) Compare boiling point of *n*-pentane and neo-pentane.

(*i*) Draw energy profile diagram for the following reaction :



(*Continued*)

GROUP – B

(*Inorganic*)

Subgroup-B(a)

Answer any **one** question : 15×1

8. (*a*) What is the origin and physical significance of magnetic quantam number ? 3

(*b*) Determine the ratio of ionisation energy of H atom, He^+ ion and Li^{2+} ion using Bohr's idea. 3

(*c*) Comment on the relative ionic radii of O^{2-}, F^- and Na^+ ions. 2

(*d*) Explain why the complex forming ability of Group-2 metal ions changes as 3

$$Be^{2+} \rangle Mg^{2+} \rangle Ca^{2+} \rangle Sr^{2+} \rangle Ba^{2+}$$

(*e*) State with reason whther there will be any increase or decrease in acidity if : 4

(*i*) Anhydrous $AlCl_3$ is added to liquid phosgene.

(*ii*) An excess solution of KI is added to HgO.

(*iii*) SbF_5 is added to anhydrous liquid HF.

(*iv*) $CuSO_4$ is added to aqueous solution of $(NH_4)_2SO_4$.

9. (*a*) Explain the effect of polarising power and polarisability on the properties of ionic compounds. 4

(*b*) Define Lattice energy of ionic solid. Frame the Born-Haber cycle for the formation of magnesium sulphide ionic solid and calculate the lattice energy of MgS(s) using the following energies (K. calmole^{-1}) 4

ΔH_f of MgS(s) = --82·2
ΔH_s of Mg(s) = +36·5
Heat of atomisation of S_8(s) = +133·2
$IP_1 + IP_2$ of Mg(g) = +520·6
$EA_1 + EA_2$ of S(g) = –72·4

(*c*) Explain why the solvation energy of K^+ ion is less, than that of F^- ion though they have identical ionic radii in KF crystal. 2

(*d*) Find out the radii of first and second Bohr orbits of Be^{3+} ion. 3
(Given radius of H atom is 0·529 Å)

(*e*) The ionisation energies for Cl^-, Cl and Cl^+ are 349, 1251 and 2300 KJ/Mole, respectively. Explain the trend. 2

Subgroup-B(b)

Answer any **two** questions : 10×2

10. (*a*) What is inert-pair effect ? Why does Thallium form iodide only in the +1 oxidation state ? 3

(*b*) Discuss the type of defect observed in the crystal of ZnO when heated ? What is the consequence of heating and cooling of ZnO ? 3

(*c*) Explain why $KHCO_3$ is less soluble in water than K_2CO_3 but it is more soluble than $NaHCO_3$. 2

(*d*) If the energy difference between the ground state and excited state of an atom is

$4{\cdot}4 \times 10^{-19}$ Joule. What is the wavelength of the photon required to produce this transition ? 2

11. (*a*) Compare the following pairs with respect to volatility and solubility in organic solvents : 2

(*i*) KCl and LiCl
(*ii*) $TiCl_2$ and $TiCl_4$

(*b*) Predict the structure of SF_4 using Bent's rule. 2

(*c*) Find out the critical radius ratio (r_{cation}/r_{anion}) of ZnS lattice using radius ratio rule. 3

(*d*) Why NaOH solution is not used as precipitating agent instead of $NH_4Cl + NH_4OH$ during the precipitation of $Fe(OH)_3$, $Al(OH)_3$ and $Cr(OH)_3$. 3

12. (*a*) The C-Cl bond distance in CH_3Cl and CF_3Cl are 1·78 Å and 1·75 Å respectively. Comment on this difference with the help of Bent's rule. 2

(*b*) Predict the direction of the following equilibria : 3

(*i*) $2CH_3MgF + HgF_2 \rightleftharpoons (CH_3)_2Hg + 2MgF_2$

(*ii*) $La_2(CO_3)_3 + Bi_2S_3 \rightleftharpoons La_2S_3 + Bi_2(CO_3)_3$

(*c*) Why Li can not form super oxide but K, Rb and Cs can form stable super oxides ? 2

(*d*) Which of the following bond angle is longer and why 3

(*i*) $H-\widehat{O}-H$ angle in H_2O and H_3O^+

(*ii*) $F-\hat{I}-F$ angle in IF_2^+ and IF_6^+

13. (*a*) The F–F bond distance in F_2 is 141·3 pm. Calculate the Allred-Rochow electronegetivity of fluorine using Slaler's rule. 3

(*b*) Berrylium chloride hydrate loses no water over P_4O_{10}. Explain. 2

(*c*) Solution of Na in liquid ammonia shows electrical conductance but conductivity decreases when solution becomes more concentrated. Explain. 2

(*d*) What are super acids ? How the acidity of such solution is measured ? Explain with example. 3

Subgroup-B(c)

Answer any **five** questions : 2×5

14. (*a*) Find the ground state term symbol for V^{3+} ion.

(*b*) Predict the shapes of CH_3^- and CF_3^+ ions with explanation.

(*c*) $MgSO_4$ is soluble in water but $BaSO_4$ is not.– Explain.

(*d*) Atomic radii of Nb and Ta are atmost identical.– Explain.

(*e*) Why Au can form CsAu ?

(*f*) The chemistry of Li is 'anamolous' in comparison with Na and K. Justify.

(*g*) Explain the linear symmetrical structure of HF_2^- ion.

(*h*) Electron affinity of Cl is greater than F yet F is much stronger oxidant than Cl. Explain.

(*i*) State the theory by which the reaction

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

may be regarded as an acid-base reaction.

(*j*) Why the shape of s-orbital is spherical ?