2016

M.Sc.

3rd Semester Examination

CHEMISTRY

PAPER—CEM-301

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Organic Special)

Answer any *five* questions,
taking at least *two* from each group.

Group—A

1. **(a)** How Hammett equation was derived with reference to ionisation of benzoic acid as standard.

(b) Define 'σ' constant and explain the difference in polar effect of the following substituent in aromatic nucleus with proper reasoning :

— NH_2 : σ_m (−0.16), σ_p (−0.66)

— OH : σ_m (+0.12), σ_p (−0.37)

— OMe : σ_m (+0.12), σ_p (−0.27)

— F : σ_m (+0.34), σ_p (+0.06) 4+4

2. (a) What is p (reaction constant) ? Explain. In alkaline hydrolysis of methyl benzoate what would be the effect of introducing $-NO_2$ group in meta or para position, where $\sigma_m NO_2 = +0.71$ and $p = 2.460$.

(b) Explain the effect of $-NO_2$ and $-NH_2$ group in para of the aromatic ring of the following reaction, where p = –0.99

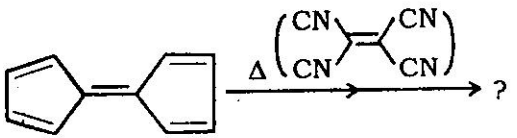
$$Aro^- + EtI \xrightarrow[EtOH]{OH^-} AroEt + I^- .$$

(c) A non-linear Hammett is obtained in the hydrolysis of ethyl benzoate with 99.9% H_2SO_4 with p = 1.4 and p = –3.2. Show the mechanistic pathways followed by the reaction with explanation. 2+2+4

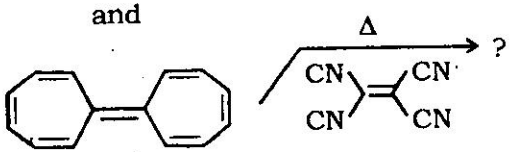
3. (a) Explain with reason why the linearity of Hammett plot is deviated in case of ionisation of nitro-phenol.

(b) Show the mechanistic path of semicarbazone formation in substituted aromatic aldehyde where pH = 1.75 and p = 0.91 in 25% ethanol at 25°C. Show the rate determing step of the reaction and indicate the type of substituent which will accelerate the reaction. 4+4

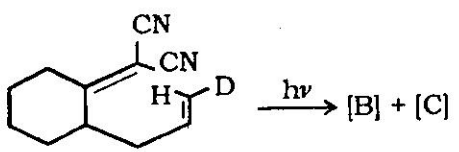
4. (a) Predict the products in the following set of reaction indicating frontier orbital interaction (F.O.I) in each case :



and



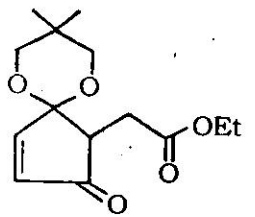
(b) Carry out the reaction and indicate the positions of 'D' in the expected products [B] and [C] (Show F.O.I) :



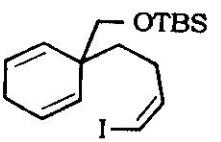
[A] 4+4

5. (a) Transition metal based organometallic compound differ from main group metal based organometallic compound —explain.

(b) Write down the structures of products (A – F) in the following reactions :

(i) 

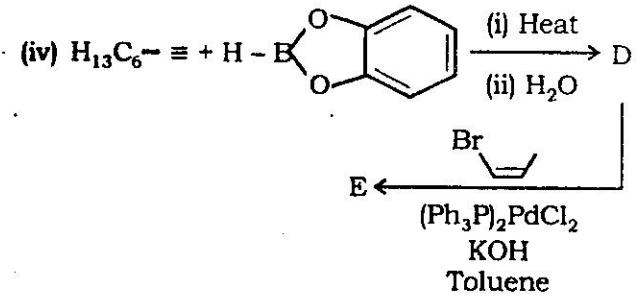
$Cp_2Ti = CH_2$ → A

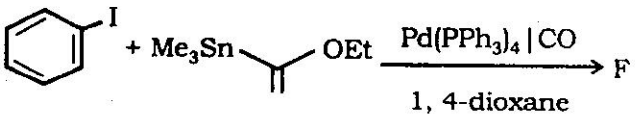
(ii) 

$Pd(OAc)_2$, (R)-BINAP, Ag_2CO_3, NMP → B

(iii) 

PhHg(OAc), $Pd(OAc)_2$ → C

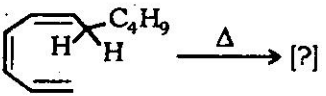
(iv) 

(v) 

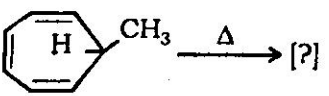
2+1×6

Group—B

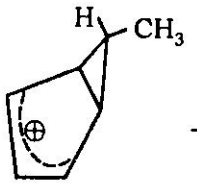
6. **(a)** **Carry out the following transformation and identify the products in each case with reason (F.O.I) :**

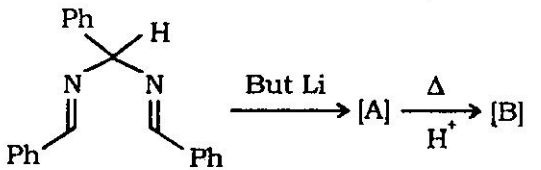


and



(b) Identify the products in the following reaction indicating F.O.I :

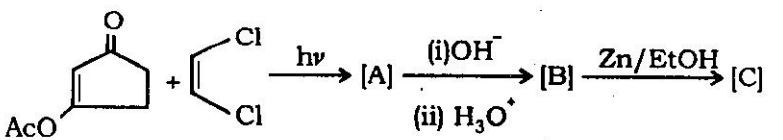
(i) 

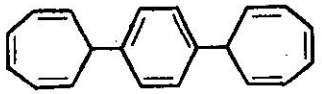
(ii) 

2×2+2×2

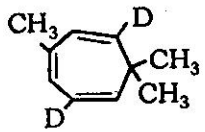
7. Identify the products in the following reaction :

(i)

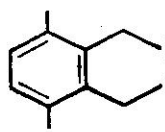
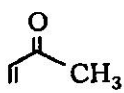


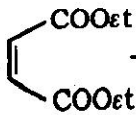
(ii)  $\xrightarrow{\Delta}$ [A] $\xrightarrow{h\nu}$ [B]

$\xrightarrow{h\nu}$ [C] $\xrightarrow{\Delta}$ [D]

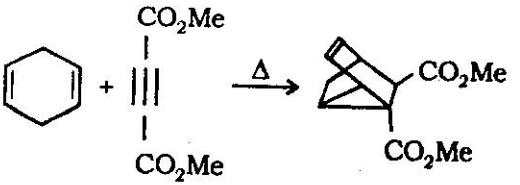
(iii)  $\xrightarrow{\Delta}$? 2+4+2

8. Identify the product in the following reaction :

(i)  $\xrightarrow[\Delta]{\text{Zn-Ag}}$ [A] $\xrightarrow{\Delta}$  [B]

(ii)  +  $\xrightarrow{\Delta}$ [A] $\xrightarrow[CH_3Br]{}$  [B] $\xrightarrow[\text{temp}]{\text{Room}}$ [C]

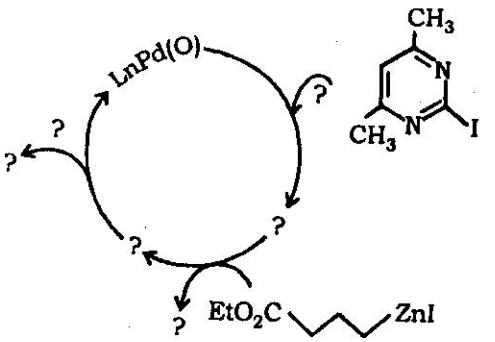
(iii) Carry out the transformation indicating products in each step :



2+2+4

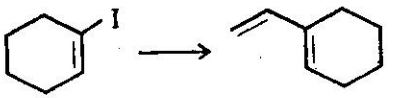
9. (a) What is the migratory insertion ? Show a migratory insertion with reference to transition metal complex.

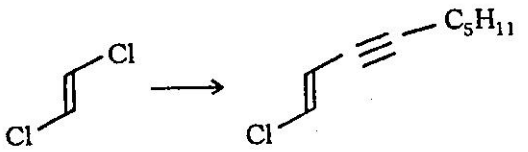
(b) Complete the following cycle

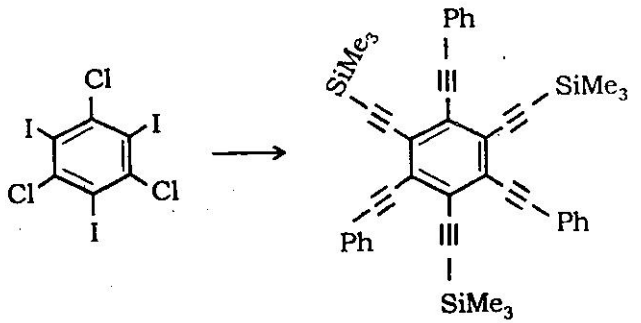


(Continued)

(c) Use appropriate organometallic reagent for the following transformation

(i) 

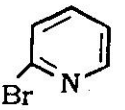
(ii) 

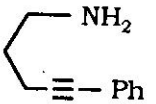
(iii) 

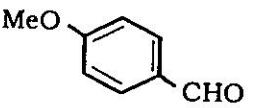
2+3+3

10. (a) Give example where hydropalladation-dehydropalladation can lead to alkene isomerisation.

(b) Predict the product of the following reaction with mechanism :

(i) $Ph - C \equiv C - H +$  $\xrightarrow[\text{CuI}\\\text{Et3N, rt}]{Cl_2Pd(PPL_3)_2}$?

(ii)  $\xrightarrow[\text{cat. amount}]{CpTiCl_2}$?

(iii)  $\xrightarrow{Rh(PPh_3)_3Cl^-}$?

2+2×3

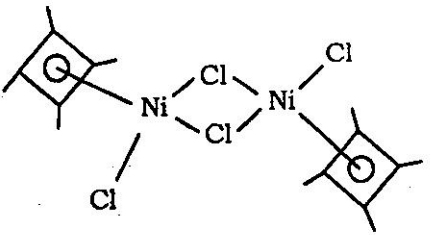
(Continued)

(*Inorganic Special*)

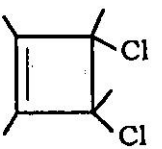
Group—A

Answer any *two* questions.

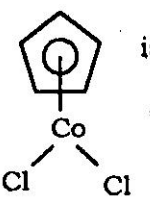
1. (a) How will you synthesize



starting

from 

? 2

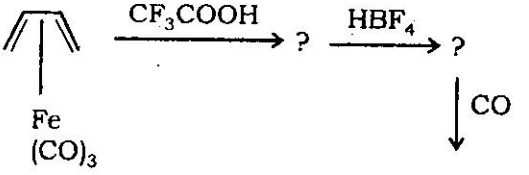
(b) What happens when 

is heated with RC ≡ CR

in Xylene ? 2

(c) '$(\eta^4 - C_4H_4)\ Fe(CO)_3$' is diamagnetic' — Discuss. 4

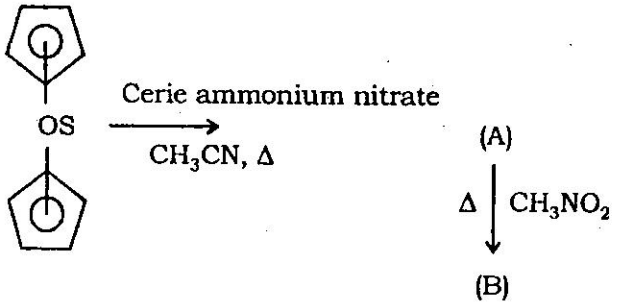
(d) Complete the following reactions :



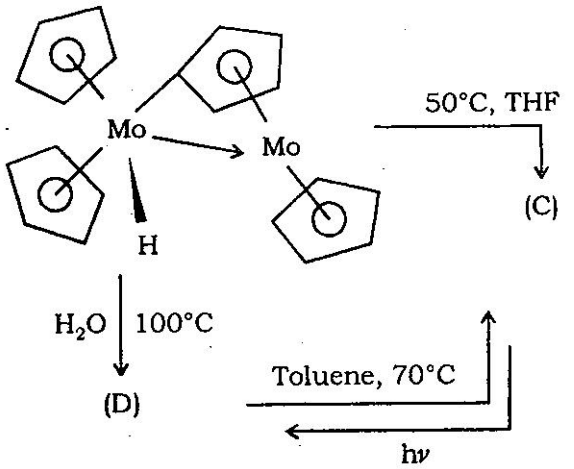
2

2. Predict products for the following reactions : 2×5

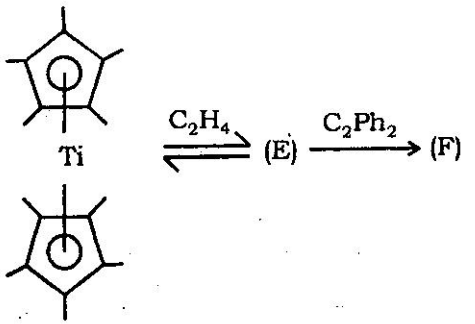
(a)

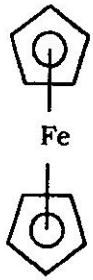


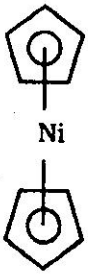
(b)



(c)



(d)  $\xrightarrow[H_3PO_4]{Ac_2O}$ (G) $\xrightarrow[\text{Phosphate}]{\text{Yeast}}$ (H)

(e)  $\xrightarrow{HBF_4}$ (J) $\xrightarrow{Cp_2Ni}$ (K)

3. (a) Draw the catalytic cycle for the following :

(i) Monsanto acetic acid process ;

(ii) Wacker Oxidation. 4+4

(b) Write down the problems associated with 'Monsanto process'. 2

Group—B

Answer any *two* questions.

4. (a) With the help of group theory determine the symmetries of possible combinations of atomic orbitals of carbon atoms which are effective for π-bond formation in cyclobutadiene. Using projection operator method find out the appropriate SALCs for these symmetries. Construct qualitative π-molecular orbital energy level diagram for cyclobutadiene molecule and explain why it is an extremely unstable molecule.

Although cyclobutadiene is unstable, (cyclobutadiene) $Fe(CO)_3$ is a stable molecule — explain.
(Given below character table and correlation table) 8

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

Correlation table

D_{4h}	C_{4v}
A_{2u}	A_1
B_{2u}	B_1
E_g	E

(b) Establish the relation $\chi_{(\alpha)} = \dfrac{\sin\left(1+\frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}}$ where the terms have usual significance. 2

5. What do you mean by "exclusion rule" ? Show that this rule is applicable for trans-N_2F_2 molecule. (Given below the character table for C_{2h} point group). 2+8

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

Or

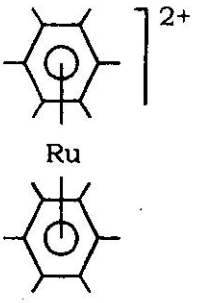
6. With the help of group theory determine the symmetries of the group of orbitals of F atoms which are effective for σ-bond formation in PF_5 molecule. Write appropriate SALCs for these symmetries. Construct a qualitative σ-bonding molecular orbital energy level diagram for PF_5 and from this energy level diagram comment about the π-acid nature of PF_5 molecule. (Given below the character table for D_{3h} point group). 3+3+3+1

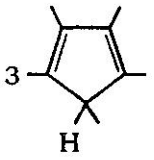
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

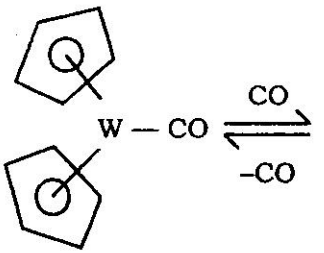
7. (a) Write down the catalytic cycle for the hydroformylation using $HCo(CO)_4$ catalyst. 4

(b) What do you mean by oxidative addition reaction ? Mention essential requirements for this process. 3

(c) Predict the product : 1×3

(i) 

(ii) 

(iii) 

(*Physical Special*)

Answer any *five* questions, taking *two* questions from Group–A & B each and *one* question from Group–C.

Group—A

Answer any *two* questions of the followings.

1. Use non-degenerate time independent perturbation theory to obtain the first order correction to wavefunction and second order correction to energy of a system. 4+4

2. (a) Calculate the first order correction to the ground state energy of a Harmonic Oscillator whose potential is,

$$U(x) = \frac{1}{2}kx^2 + \frac{1}{6}vx^3 + \frac{1}{24}bx^4$$

Given,

zero order wave function of H.O

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$$

where $\alpha = \left(\frac{k\mu}{\hbar^2}\right)^{1/2}$

and, $\int_0^{\alpha} x^{2m}\, e^{-\alpha x^2} dx = \frac{(2m-1)!}{2^{m+1} a^m}\left(\frac{\pi}{a}\right)^{1/2}$

(b) The unperturbed wave function for the infinite square well is given by $\psi_n^{(0)} = \sqrt{\frac{2}{a}}\, \mathrm{Sin}\left(\frac{n\pi}{a}x\right)$.

Suppose one perturbs the system by simply raising the floor of the well a constant amount V_0. Find the first order correction to energy. 5+3

3. Transition probability from state $\psi_a \rightarrow \psi_k$ is defined as,

$$P_{a\to k}(t, w_{ka}) = \left| C_K^{(1)}(t) \right|^2$$

where, $C_k^{(1)}(t) = \frac{1}{i\hbar}\int_0^t H'_{ka}(t)\, e^{iw_{ka}t'} dt'$

Use H' as an oscillating perturbation and hence deduce the integrated expression of the transition probability. Comments on your result. 6+2

Group—B

Answer any *two* questions of the followings.

4. (a) Use $\psi = c_1x(x-1) + c_2x^2(x-1)^2$ as trial wave function for particle in a one dimensional box of unit length and hence deduce the ground state energy using variational principle. Compare your result with the exact energy of the problem.

(b) The trial wave function of a system is expanded as,

$$\psi_t = C_1\phi_1 + C_2\phi_2$$

The matrix elements of the Hamiltonian are,

$$\langle\phi_1|H|\phi_1\rangle = 0$$

$$\langle\phi_1|H|\phi_2\rangle = \langle\phi_2|H|\phi_1\rangle = 2$$

$$\langle\phi_2|H|\phi_2\rangle = 3$$

Find the approximate ground state energy of the system from the linear variational principle. 5+3

5. Use Hückel theory to obtain energy and wave functions for π-MO of Allyl radical. Write down the co-efficient matrix of π-MO for Allyl radical and hence obtain the π-electron density on carbon atom. 4+4

6. (a) Deduce the expression of Fermi Golden rule. Comments on the expression.

(b) A two level unperturb system is described by the following Hamiltonian,

$$H_0 = \begin{pmatrix} 1 & 0 \\ 0 & 4 \end{pmatrix}$$

Now a small perturbation is switched on and is represented by

$$V = \begin{pmatrix} a & c \\ c & b \end{pmatrix}$$

Find the energy of the ground state upto second order correction. 5+3

Group—C

Answer *one* question of the followings.

7. Write down the steps involved for the determination of Symmetry of vibrational modes of linear molecules using Integration method.

Obtain the Symmetry of vibrational modes of HCN using Integration method.

Character table of $C_{\alpha v}$ point group is given below :

	E	$2C_\alpha^\theta$	$2C_\alpha^{\theta+d\theta}$	$....\alpha\sigma_v$		
A_1	1	1		1	z	x^2+y^2, z^2
A_2	1	1		−1	R_z	
E_1	2	$2Cos\theta$		0	(x, y), (R_x, R_y)	(xz, yz)
E_2	2	$2Cos2\theta$		0		x^2-y^2, xy
E_3	2	$2Cos3\theta$		0		

2+6

8. Use group theoretical principle to obtain the state of hybridization of central atom in $[PtCl_4]^{2-}$.

Obtain the hybrid orbitals as the linear combination of atomic orbitals.

Character table of D_{4h} point group is given below :

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

4+4