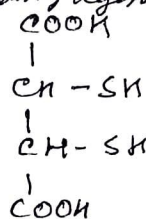Ans1a) The basic requirements of a chelating ligand to be considered for 'chelation Therapy' are:

• Conditional stability constant: It binds with toxic metal sufficiently strongly to compete with the endogenous biological ligands such as proteins.

• Lipophilicity of the chelating drugs: It has to be sufficiently lipophilic, (i.e; the ability of a chemical compound to dissolve in fats, oils, lipids and non-polar solvents) to penetrate the lipid membranes to reach the body compartment where the toxic metal is accumulated.

• Hard and soft Acids and Bases theory and selection of chelating drugs: To remove a hard toxic metal ion, a chelating drug with hard donor sites is preferred, and to detoxify a soft metal, the chelating drug should have the soft binding sites.

• Designing of antidotes with the binding sites mimicking the endo-genous binding sites: The binding sites of the chelating drugs should be similar to endogenous binding sites.

• Must not ~~bind~~ bind with Ca and Mg which are relatively abundant and essential for human body.

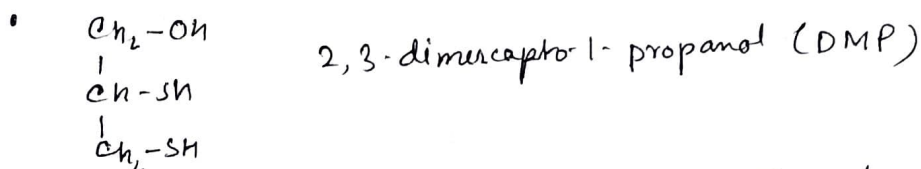• Toxic effect of the chelating drug: The administered should not be toxic and must have higher LD_{50} value.

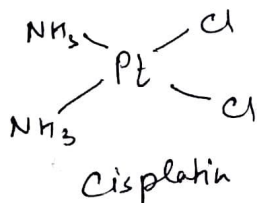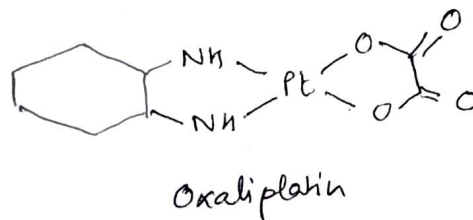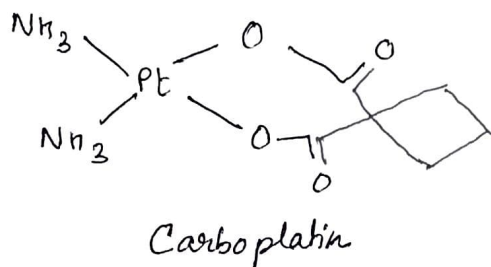Ans1b) • Chelating agent which can remove $Cu(II)$ from body:

```
  COOH
   |
  CH - SH
   |
  CH - SH
   |
  COOH
```

2,3-dimercapto succinic acid (DMSA)

- CH_2-SO_3Na
  $\,\,\,|$
  $CH-SH$
  $\,\,\,|$
  CH_2-SH

  Sodium 2,3-dimercapta propane-1-sulphonate (DMPS)

- CH_2-OH
  $\,\,\,|$
  $CH-SH$
  $\,\,\,|$
  CH_2-SH

  2,3-dimercapto 1-propanol (DMP)

c) Platinum complexes used in cancer chemotherapy and y are:

Carboplatin

Oxaliplatin

Cisplatin
[Cis-dichlorodiammine platinum(II)]

Nedaplatin

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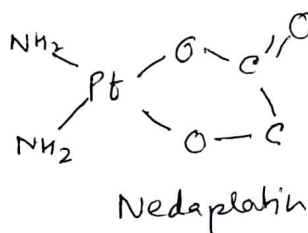- G Suite ID: 2020ITB065.tathagata@students.iiests.ac.in
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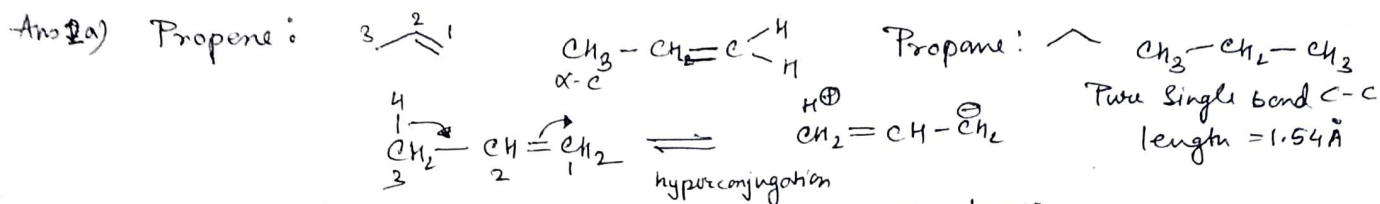
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Ans 2a) Propene: $3\diagup\diagdown^{2}_{1}$

$CH_3 - CH = C <^H_H$
$\alpha - c$

Propane: $\diagup\diagdown$ $CH_3 - CH_2 - CH_3$
Two Single bond C-C
length = 1.54 Å

$\underset{3}{CH_2} - CH = \underset{1}{CH_2}$ ⇌ $\overset{H^\oplus}{CH_2} = CH - \overset{\ominus}{CH_2}$
hyperconjugation

∴ 3 α-H , ∴ 3 hyperconjugative structures

∴ Partial double bond character is developed in $C2 - C3$ atoms. Bond order increases, hence decreasing bond length.

Hence in propene the $C_2 - C_3$ bond length is 1.48 Å whereas in propane it is 1.54 Å.
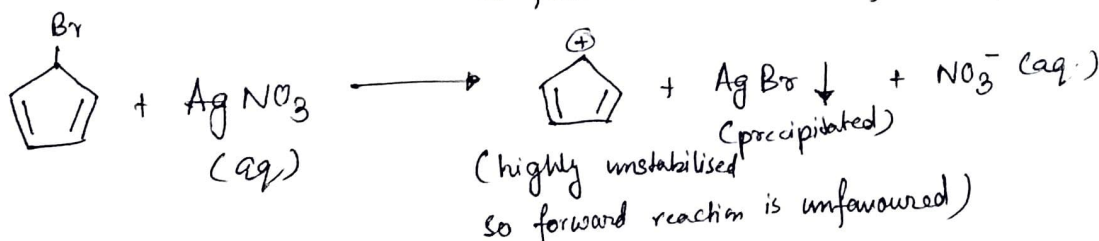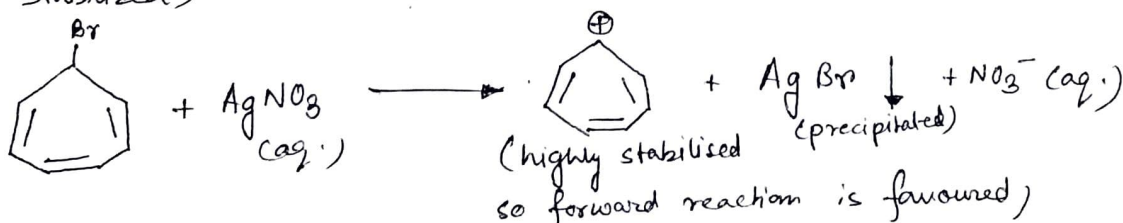
b)

A   B
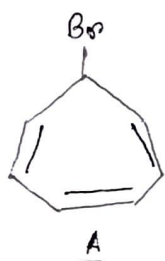
AgBr precipitation on addition of aq. $AgNO_3$ soln, take place only if Br^- is formed from A and B. Hence we get Br^-,
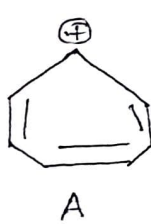
The ion from A and B are: hence we can conclude that A is far more stable than B hence produced very quickly.
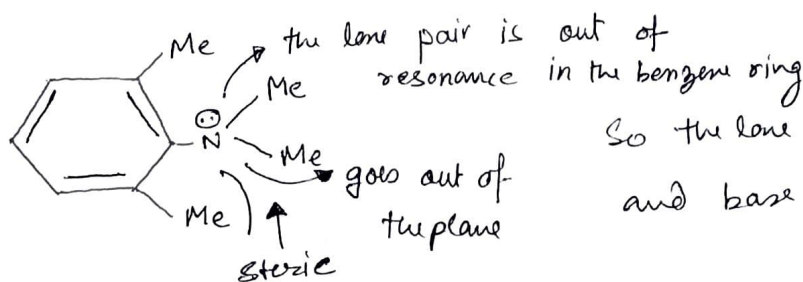
A
• planar structure
• (4n+2) πe^-s, Huckel's Rule
• Aromatic ion (hence highly stabilized)

B
• planar structure
• (4n) πe^-s, Huckel's Rule
• Anti-aromatic ion (Hence highly destabilized)

$+ AgNO_3$ (aq.) ⟶ + Ag Br ↓ (precipitated) + NO_3^- (aq.)
(highly stabilised so forward reaction is favoured)

$+ AgNO_3$ (aq) ⟶ + Ag Br ↓ (precipitated) + NO_3^- (aq.)
(highly unstabilised so forward reaction is unfavoured)

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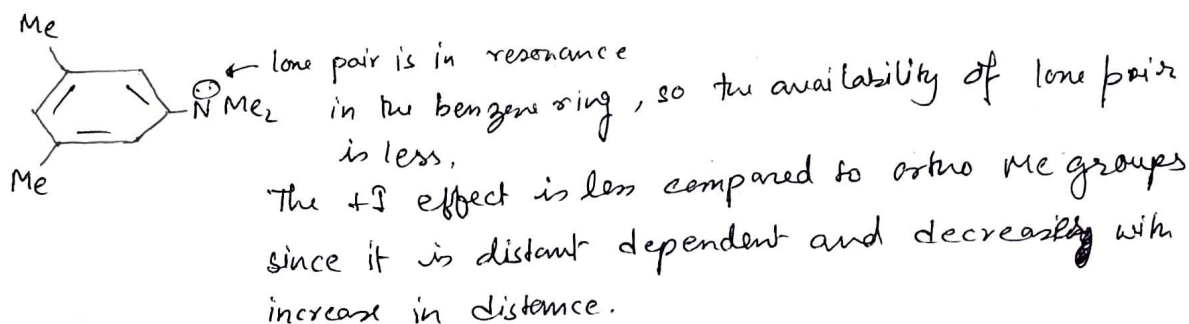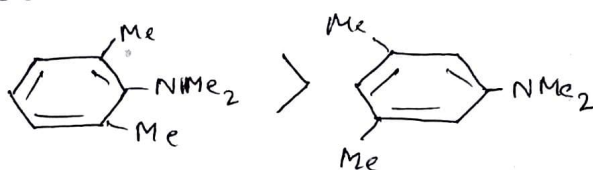- Number of Sheets uploaded: 7

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c)

the lone pair is out of resonance in the benzene ring

goes out of the plane

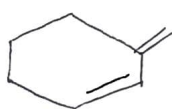steric hindrance

So the lone pair is more available and base means electron donors.

$-CH_3 (Me)$ are $+I$ groups and are distance dependent and being at ortho position, it increases the electron density at $\overset{\cdot\cdot}{N}$.

lone pair is in resonance in the benzene ring, so the availability of lone pair is less.

The $+I$ effect is less compared to ortho Me groups since it is distant dependent and decreasing with increase in distance.

∴ The basicity of

d)

Base value of acyclic conjugated dienes	= 215 nm
Exocyclic double bond	= 5nm
2 alkyl substituent	= (2×5)nm =10 nm
$+$	
λ_{max}	= 230 nm
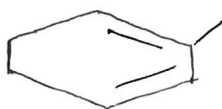
Base value of homoannular conjugated dienes	= 253 nm
3 alkyl substituent	= (3×5)nm = 15nm
$+$	
λ_{max}	= 268nm

Since the λ_{max} for two compounds are different, thus by UV spectroscopy the above mentioned compounds can be distinguished.
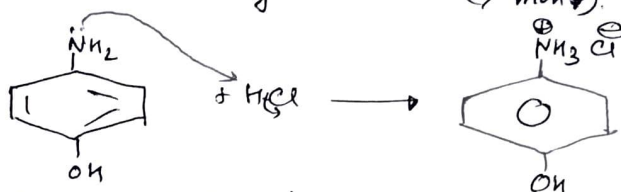
And 2d) λ_{max} of aq. soln of para-aminophenol shows blue shift (hypsochromic) when the solution is acidified with dilute HCl :

• the lone pair of amine is blocked by acidic hydrogen from dil. HCl and hence the conjugation of lone pair with π bond system of benzene ring is blocked hence the energy gap increases and the energy absorbed is high, so the wave length decreas ($\lambda_{max}\downarrow$).

• Due to presence of auxochrome '-OH' also leads to blue shift. in para aminophenol.

Ans 3a) The reactions of higher molecularity (or order $\geqslant 3$) are rare because according to collision theory, more than 2 molecules come rarely together (probability is very low), so the probability of their occurrence is very less. ~~change~~ chances of interaction of 3 particles or more is very low at any point of time, and reaction takes place by collision so having higher molecularity is much ~~for~~ rare event.

b) $B \xleftarrow{k_1} A \xrightarrow{k_2} C$ Let us consider two competing (parallel) irreversible first order processes as: $A \xrightarrow{k_2} C$ and $A \xrightarrow{k_1} B$

The rate law:

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$\Rightarrow \frac{d[A]}{dt} = -(k_1 + k_2)[A]$$

$$\Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -(k_1+k_2)\,dt$$

$$\Rightarrow \ln\left|\frac{[A]}{[A]_0}\right| = -(k_1+k_2)t$$

$$\Rightarrow [A] = [A]_0\, e^{-(k_1+k_2)t}$$

Rate of change of $[B] = \frac{d[B]}{dt} = k_1[A] = k_1[A]_0\, e^{-(k_1+k_2)t}$

Integrating this equation with condition at $t=0$, ~~$[B]_0$~~ $[B]_0 = 0$
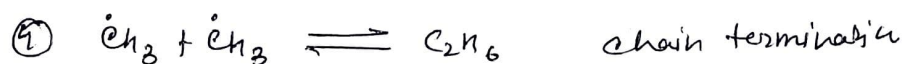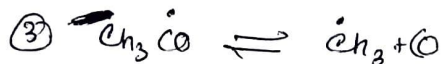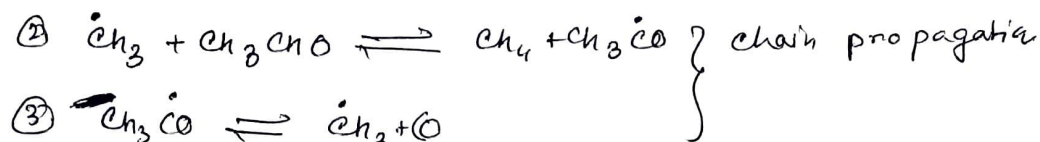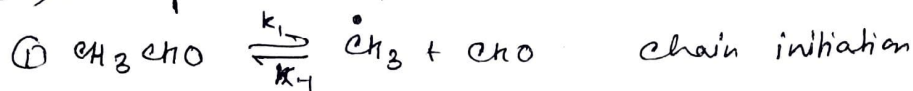
Thus $\boxed{[B] = \dfrac{k_1[A]_0}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right)}$ (P)

~~Simply f~~ Similarly, $\frac{d[C]}{dt} = k_2[A]$

$$\boxed{[C] = \frac{k_2[A]_0}{k_1+k_2}\left(1 - e^{-(k_1+k_2)t}\right)}$$

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Ans 3c) Decomposition of acetaldehyde:

① $CH_3CHO \underset{K_4}{\overset{k_1}{\rightleftharpoons}} \dot{C}H_3 + CHO$ chain initiation

② $\dot{C}H_3 + CH_3CHO \rightleftharpoons CH_4 + CH_3\dot{C}O$ } chain propagation

③ $CH_3\dot{C}O \rightleftharpoons \dot{C}H_3 + CO$ }

④ $\dot{C}H_3 + \dot{C}H_3 \rightleftharpoons C_2H_6$ chain termination

The steady-state approximation may be applied for reaction intermediates, CH_3 and CH_3CO radicals, their concentration remains almost constant.

$\therefore \dfrac{d[CH_3]}{dt} = 0 = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO]$
$$- k_4[CH_3]^2 \quad \cdots \quad ①$$

and $\dfrac{d[CH_3CO]}{dt} = 0 = k_2[CH_3]\{[CH_3CHO] - k_3[CH_3CO] \quad \cdots ②$

① + ② ;
$$k_1[CH_3CHO] = k_4[CH_3]^2$$

$$\Rightarrow [CH_3] = \left(\frac{k_1}{K_4}[CH_3CHO]\right)^{1/2}$$

Rate of formation of methane i.e; rate of decomposition of acetaldehyde is

$$Rate = \frac{d[CH_4]}{dt} = k_2[CH_3][CH_3CHO]$$
$$= k_2\left(\frac{k_1}{k_4}\right)^{1/2}[CH_3CHO]^{3/2}$$

Decomposition thus follows order as 3/2.

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1)

$$\frac{d[B]}{dt} = k_1 [A]_0 e^{-(k_1+k_2)t}$$

$$\Rightarrow \int_0^{[B]} d[B] = k_1 [A]_0 \int_0^t e^{-(k_1+k_2)t}$$

$$\Rightarrow \left[[B] \right]_0^{[B]} = \frac{k_1 [A]_0}{k_1+k_2} \left[-e^{-(k_1+k_2)t} \right]_0^t$$

$$\Rightarrow [B] = \frac{k_1 [A]_0}{k_1+k_2} \left(1 - e^{-(k_1+k_2)t} \right)$$