Indian Olympiad Qualifier in Chemistry (IOQC) 2020-2021

conducted jointly by

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

and

Indian Association of Physics Teachers (IAPT)

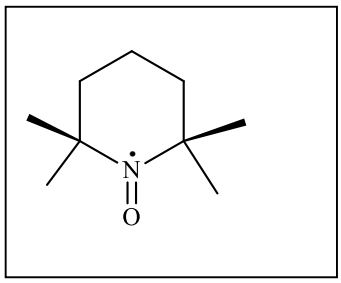
Part II: Indian National Chemistry Olympiad (INChO)

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

Problem 1 — 18 marks

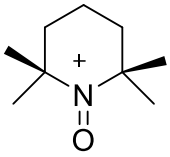
Persistent radical – TEMPO

1.1

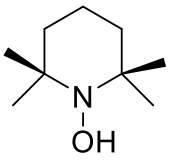


1.2

A = TEMPO$^+$



B = TEMPOH



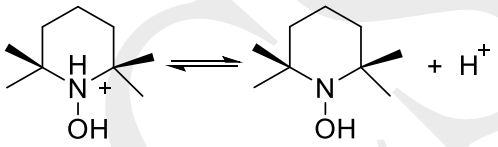
1.3

TEMPO + H^+ + $e^- \rightarrow$ **B**

$$E = E^0 - 0.059\log\frac{[\text{B}]}{[\text{TEMPO}]} - 0.059\text{pH}$$

1.4

C = TEMPHOH$^+$



B **C**

1.5

Transformation at line 3 can be represented as

TEMPO + $2H^+$ + $e^- \rightarrow$ C

$$E = E^0 - 0.059\log\frac{[\text{C}]}{[\text{TEMPO}]} - (0.059 \times 2)\,\text{pH}$$

Hence ratio of the slope of segment 3 to that of segment 2 is **2:1**

1.6

The disproportionation reaction is given by:

$2\text{TEMPO} + 2H^+ \rightleftharpoons \text{TEMPO}^+ + \text{TEMPHOH}^+$ (1)

$\text{TEMPO} \rightleftharpoons \text{TEMPO}^+ + e^-$ (E^o = – 0.745 V) (2)

$\text{TEMPO} + H^+ + e^- \rightleftharpoons \text{TEMPOH}$ (E^o = 0.610 V) (3)

$\text{TEMPOH} + H^+ \rightleftharpoons \text{TEMPHOH}^+$ (pK_a = 7.4) (4)

$\Delta G°_{(1)} = \Delta G°_{(2)} + \Delta G°_{(3)} + \Delta G°_{(4)}$

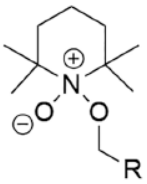
K = 1.31×10^5

1.7

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$

Working electrode is the anode and counter electrode is the cathode.

1.8



1.9 a) i) pH < 7

B + **A** ⇌ 2TEMPO + H^+

OR

B ⇌ **C** + H^+ **and C + A** ⇌ 2TEMPO

ii) pH > 7

B ⇌ TEMPO + e^- and

B ⇌ **C** + H^+ and **C** + **A** ⇌ 2TEMPO

b) Case ii); conversion of **B** to TEMPO predominantly undergoes electrochemically at the applied potential, without additional consumption of **A**.

1.10 4-carboxy TEMPO

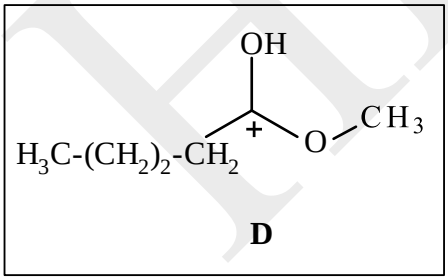
1.11 4-carboxy TEMPO < 4-hydoxy TEMPO < 4-amino TEMPO

Note that the amino functional group undergoes protonation at pH~7.

Problem 2 — 14 marks

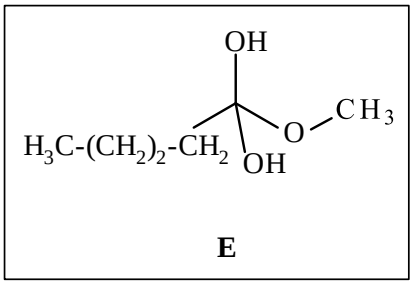
Esters

2.1 i)

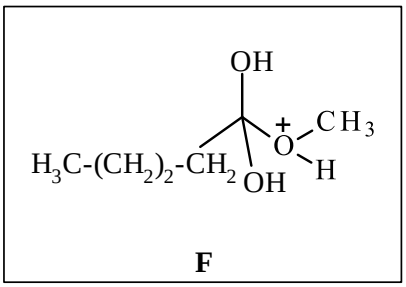


D

ii)



E

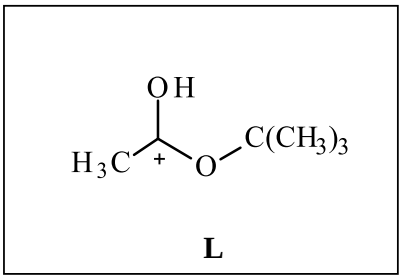


F

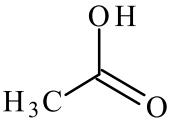
H^+

G

2.2 i)

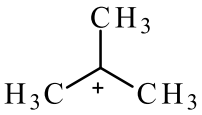


L

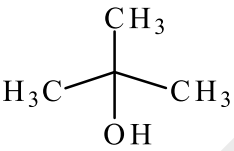


M

Cationic Intermediate



N

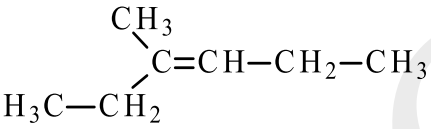


P

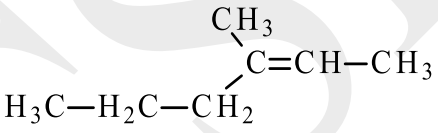
ii) Step 2

iii) $A_{AL}1$

2.3 i)

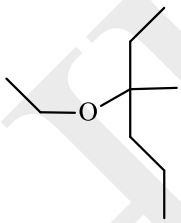


R



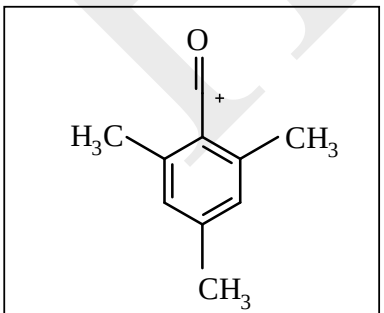
S

ii)



T

2.4



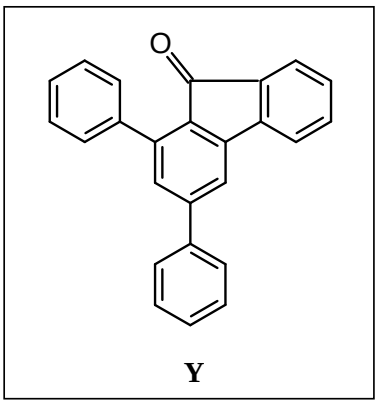
V

Cationic intermediate

CH_3OH

W

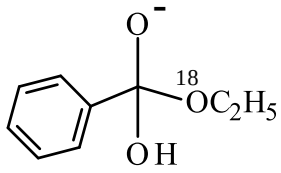
2.5



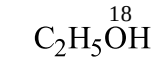
Y

2.6 i)

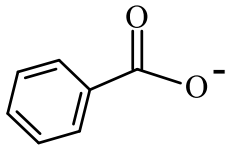
Intermediate



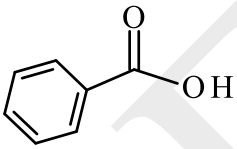
Z_1



Z_2



Z_3



Z_4

ii) $B_{AC}2$

Problem 3 — 16 marks

Ozone in Troposphere

3.1

a: CO_2 **b**: $H^{\bullet}$ **c**: O_2 **d**: NO_2 **e**: $OH^{\bullet}$

Net reaction from steps i to v: $CO + 2O_2 \rightarrow CO_2 + O_3$

3.2

i) correct.

Statement **S1-S5**	Supporting facts (**R1-R7**)	Supporting Graph(s) (**G1-G9**)
S2	**R1**	**G6, G9 / G4, G7**
S5	**R6**	**G1, G4, G7 / G3, G6, G9**

ii) incorrect.

Statement **S1-S5**	Supporting facts (**R1-R7**)	Supporting Graph(s) (**G1-G9**)
S1	**R4**	**G5, G8**
S3	**R2, R7**	**G1, G3**
S4	**R7, R1**	**G7, G9**

3.3

$O_3 + 2H^+ + 2I^- \rightarrow I_2 + O_2 + H_2O$,

$I_2 + I^- \rightarrow I_3^-$

1 mol O_3 = 1 mol I_3^-

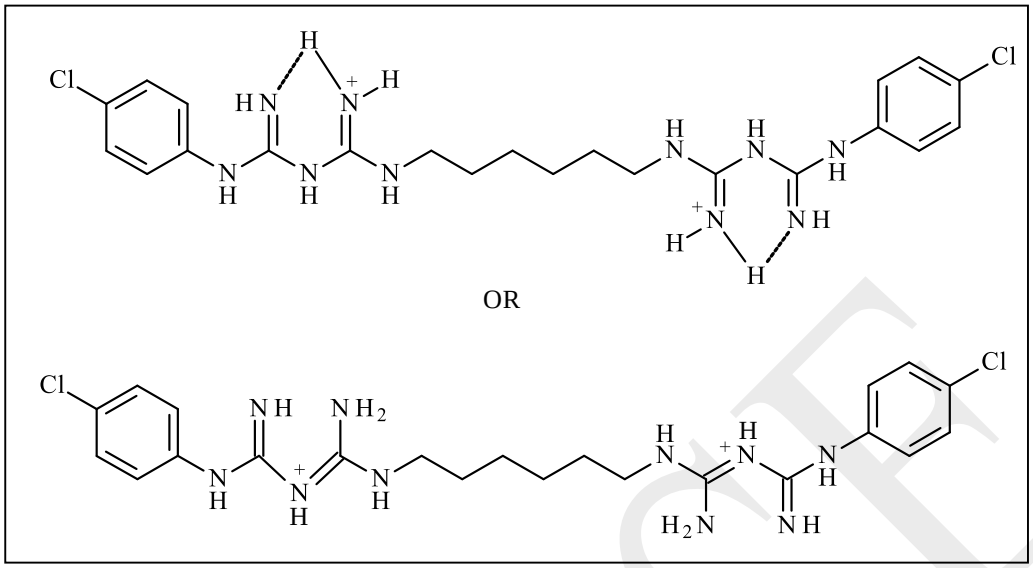
Moles of I_3^- produced = 2.6×10^{-8} mol

Concentration of ozone by mass = **211 ppb**

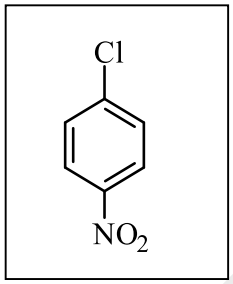
Problem 4 — 22 marks

Chlorhexidine

4.1



4.2



4.3

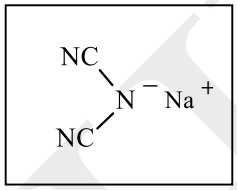
a. [X]

b. [ ]

c. [ ]

d. [ ]

4.4



4.5

For acetate salt: $ChH_2A_2 \rightleftharpoons [ChH_2^{2+}] + 2A^-$

$K_{sp} = [ChH_2^{2+}]\,[A^-]^2$, **Solubility of ChH_2A_2, s = 0.037 mol/L**

$A^- + H^+ \rightleftharpoons HA$

$(0.074 - x)\ (10^{-7} - x)/x = 1.75 \times 10^{-5}$

$x << 0.074$

4.6

Typical aggregate size at this concentration is 2500/898 ~ **3 units**

4.7

(i) 1% solution of NaCl = 10.0/58.44 = 0.17 M.

Ksp = $[ChH_2^{2+}][Cl^-]^2$

Since concentration of ChH_2G_2, s<< 0.17

$2.1 \times 10^{-9} = [s][2.89 \times 10^{-2}]$

Thus chloride salt will precipitate and effective concentration of ChH_2G_2 in NaCl solution, s = 0.72×10^{-7} mol/L.

Effectiveness will decrease.

(ii) 0.1% solution of ChH_2G_2 = 1/898 = 0.0011 M

Concentration of acetate ions, x in 0.9 M Acetic acid solution is given by

$x^2 / (0.9 - x) = 1.76 \times 10^{-5}$

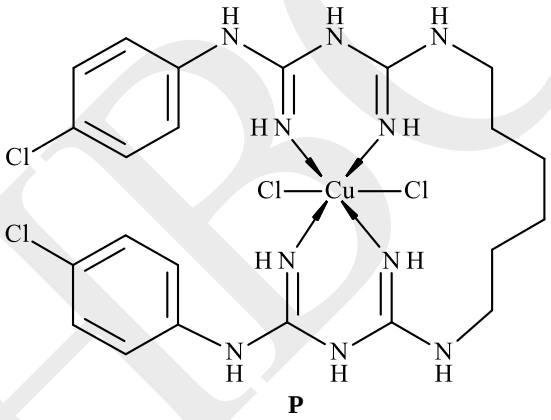
Ionic product $[ChH_2^{2+}][A^-]^2 = 0.0011 \times 0.0039 \times 0.0039 = 1.67 \times 10^{-8}$ which is much less than solubility product of Ch acetate.

Effectiveness will not decrease.

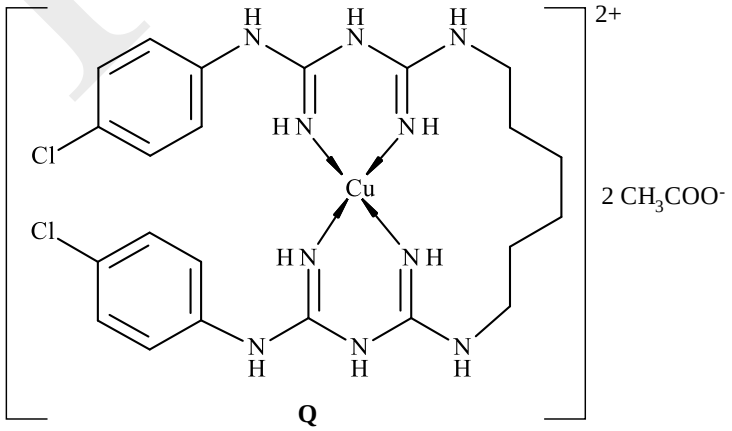
4.8 b & d, a & e

4.9 NH_2COOH

4.10

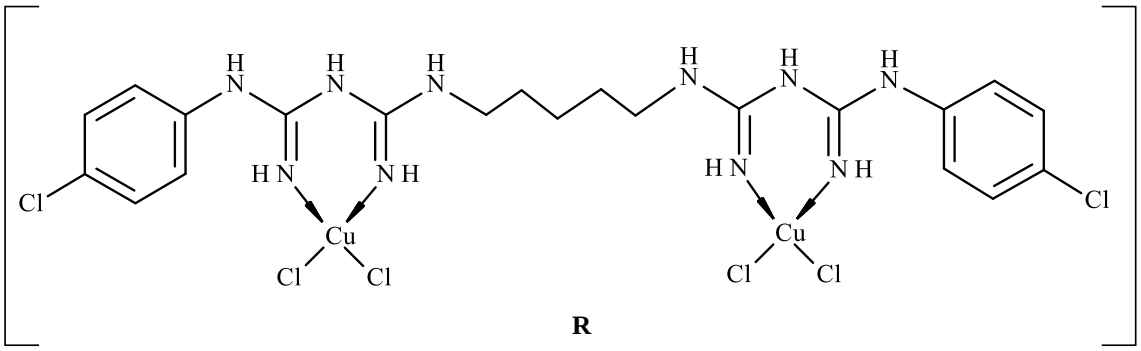


P



Q

4.11



R

Problem 5 9 marks

Helium in Rocks

5.1

Since mass number changes only in α-particle emission,

helium nuclei produced = 8.

5.2

The decay schemes are as follows-

1. $^{238}U \rightarrow 8\ ^{4}He + {}^{206}Pb$
2. $^{235}U \rightarrow 7\ ^{4}He + {}^{207}Pb$
3. $^{232}Th \rightarrow 6\ ^{4}He + {}^{208}Pb$

The relative production rates $^{238}U : {}^{232}Th : {}^{235}U$

$8 \times [^{238}U] \times k_{238} : 6 \times [^{232}Th] \times k_{232} : 7 \times [^{235}U] \times k_{235}$

= 24.8: 5.99: 1 = **25: 6: 1**

5.3

At STP, He production rate from 1 g $^{238}U = 12.72 \times 10^{-8}\ cm^3\ yr^{-1}$

Similarly, He production rate from 1g $^{232}Th = 3.15 \times 10^{-8}\ cm^3\ yr^{-1}$

Similarly, He production rate from 1g $^{235}U = 0.52 \times 10^{-8}\ cm^3\ yr^{-1}$

Assuming He production rate is constant over the entire residence time,

Residence time of water = Amount of He found per g of rock/ Production rate of He per g of rock

= **953314 years**