EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2023
General Certificate of Education Advanced Level
Higher 3

CANDIDATE NAME	

CIVICS GROUP	**2**	**2**	**–**			INDEX NUMBER		

CHEMISTRY

Paper 1

9813/01

22 September 2023

2 hours 30 minutes

Candidates answer on Question Paper.
Additional Materials: Data Booklet
Insert

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staplers, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **two** questions.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Section A	
1	**/ 20**
2	**/ 11**
3	**/ 16**
4	**/ 13**
Section B	
5	**/ 20**
6	**/ 20**
7	**/ 20**
Total	**/ 100**

This document consists of **48** printed pages.

Section A

Answer **all** the questions in this section.

1 **(a)** Carbon dioxide is the primary but not the sole contributor to the carbon reserve in the atmosphere.

(i) Name another greenhouse gas which contributes to the carbon reserve and state one source of this gas. [2]

(ii) Assume that the carbon reserve in the atmosphere is fully in the form of CO_2, and that the composition of dry air by volume is 78.08% N_2, 20.95% O_2, 0.93% Ar and 0.04% CO_2. Use the data in Fig. 1.1 to estimate the mass of the Earth's atmosphere, in kg. [2]

(i) Methane

Any one:

- roduced by domestic livestock as part of their normal digestive process.
- roduced during the storage and management of animal manure
- roduction, processing, storage, transmission, distribution, and use of natural gas
- roduction, refinement, transportation, and storage of crude oil
- enerated in landfills as waste decomposes
- enerated in the treatment of wastewater

(ii) mass of 1 mol of air $= \frac{78.08}{100} \times 28.0 + \frac{20.95}{100} \times 32.0 + \frac{0.93}{100} \times 39.9 + \frac{0.04}{100} \times 44.0$

(b) **(i)** State the main way CO_2 is captured by the soil sink. [1]

(ii) What is the main cause for the rapid increase in concentration of CO_2 since 1750, which also resulted in a decrease in the Earth's carbon reserve? [1]

(iii) Assuming that the anthropogenic CO_2 emission remains the same as that in 2022 shown in Fig. 1.1, use your answer to **(a)(ii)** to calculate the expected concentration of CO_2, in ppm, by the end of 2023.

Use a value of 4.15×10^{16} kg for the mass of the Earth's atmosphere if you are not able to calculate one in **(a)(ii)**. [3]

(i) Through **photosynthesis** where CO_2 is converted into **carbohydrates** in plants and trees.

(ii) Burning of fossil fuels for energy generation.

(iii) mass of C added to the atmosphere in one year $= \frac{46.4}{100} \times 11.2 = 5.20$ GtC

$$\text{amount of } CO_2 \text{ per year} = \text{amount of C per year} = \frac{5.20 \times 10^{12} \times 10^{3}}{12.0}$$

$$= 4.333 \times 10^{14} \text{ mol}$$

$$\text{amount of air in atmosphere} = \frac{5.278 \times 10^{18} \times 10^{3}}{28.955} = 1.823 \times 10^{20} \text{ mol}$$

$$[CO_2] = \frac{(418.6 \times 10^{-6}) \times (1.823 \times 10^{20}) + 4.333 \times 10^{14}}{1.823 \times 10^{20} + 4.333 \times 10^{14}} \times 10^{6}$$

$= \underline{\textbf{421ppm}}$

(c) The Earth's oceans provide a huge CO_2 sink to capture CO_2.

(i) Using the concentration of CO_2 in the atmosphere and Henry's Law, calculate the concentration of CO_2, in mol dm^{-3}, in seawater in 2022, with the following information.

average seawater temperature = 20 °C
density of seawater = 1.024 g cm^{-3}
molar mass of seawater = 18.28 g mol^{-1} [3]

In view of the pH of the ocean, the [CO_2(aq)], which is taken to be the [H_2CO_3*], contributes only 1% to the DIC. Use Fig. 1.2(a) to estimate

(ii) the pH of seawater, [1]

(iii) the K_a of HCO_3^-. [1]

With global warming, the temperature of seawater is also increasing.

(iv) With reference to equilibrium 1 and Henry's Law, describe and explain the effect of this on the function of the Earth's ocean as a sink for the CO_2. [2]

(i) $p_{CO_2} = 418.6 \times 10^{-6} \times 101325 = 42.415 \text{ Pa}$

At 20 °C (293 K),

$$\ln\left(K_H/10^6 \text{ Pa}\right) = -6.8346 + \frac{1.2817\times10^4}{293} - \frac{3.7668\times10^6}{293^2} + \frac{2.997\times10^8}{293^3} = 4.9471$$

$$K_H = e^{4.9471}\times10^6 \text{ Pa} = 1.4077\times10^8 \text{ Pa}$$

$$p_{CO_2} = K_H\chi_{CO_2}$$

$$42.415 = \left(1.4077\times10^8\right)\chi_{CO_2}$$

$$\chi_{CO_2} = 3.013\times10^{-7}$$

In 1 dm^3 of solution, $n_{H_2O} = \dfrac{1.024\times1000}{18.28} = 56.0175 \text{ mol}$

$$\chi_{CO_2} = \frac{n_{CO_2}}{n_{CO_2}+n_{H_2O}}$$

$$3.013\times10^{-7} = \frac{n_{CO_2}}{n_{CO_2}+56.0175}$$

$$n_{CO_2} = \frac{56.0175\times3.013\times10^{-7}}{1-3.013\times10^{-7}}$$

$$= 1.69\times10^{-5} \text{ mol}$$

[CO_2(aq)] = **<u>1.69 × 10^{-5} mol dm^{-3}</u>**

(ii) **8.2 (Note that 8.1 and 8.15 are also acceptable.)**

(iii) pK_a = pH when $[HCO_3^-] = [CO_3^{2-}]$

pK_a = 10.0

K_a = **1.00×10^{-10} mol dm^{-3}**

(iv) **K_H increases with temperature**, the position of equilibrium 1 favours the **left hand side**, rendering the ocean a **less efficient sink** for CO_2.

Question 1 continues on the next page

(d) In electrochemistry, a Pourbaix diagram, is a plot of possible thermodynamically stable phases (*i.e.*, at chemical equilibrium) of an aqueous electrochemical system. Boundaries (50 %/50 %) between the predominant chemical species are represented by lines. The Pourbaix diagram for water is shown in Fig. 1.4.

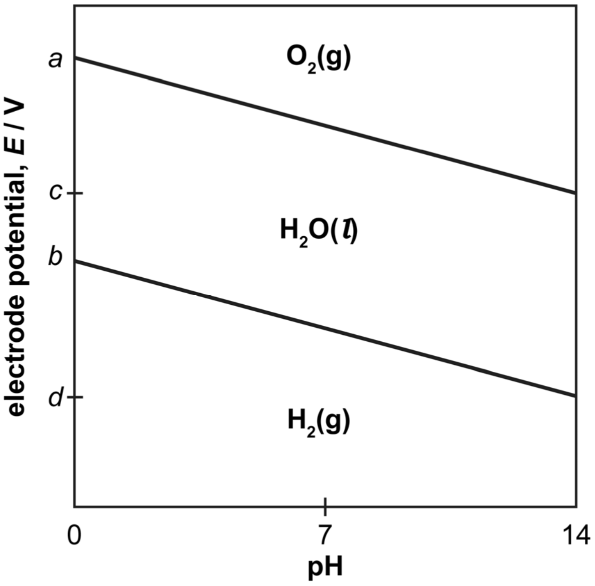


Fig. 1.4

(i) Use the *Data Booklet* to suggest values for *a*, *b*, *c,* and *d* in Fig. 1.4, by considering the redox species involved. [2]

(ii) Using your answer to **(d)(i)**, calculate the cell voltage required to operate the electrolytic cell in Fig. 1.3 with an extreme pH gradient, that is, pH 0 at anode and pH 14 at cathode. [1]

(iii) Suggest one potential problem when using seawater to capture CO_2(g) instead of pure water, with the electrolytic cell in Fig. 1.3. [1]

(i) *a* **= +1.23** for $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$

b **= 0** for $2H^+ + 2e^- \rightleftharpoons H_2$

c **= +0.40** for $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$

d **= –0.83** for $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$

(ii) $\text{cell voltage} = |E_{\text{cell}}| = |E^\ominus(H_2O|H_2) - E^\ominus(O_2|H_2O)| = |-0.83 - 1.23|$

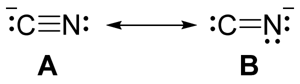
$= \underline{\mathbf{+2.06\ V}}$

(iii) Oxidation of Cl^- to Cl_2 at the anode, which is corrosive. *or*

Precipitation of $Mg(OH)_2$ or $Ca(OH)_2$ at the cathode, which coats the cathode.

[Total: 20]

2 **(a)** Cyanide ions, CN^-, has two possible resonance structures.



With reference to the structure and relative stability of each possible resonance structure, explain full

In **B**, while it is preferred that the **negative charge resides on the more electronegative N atom**, **the carbon atom is electron deficient**. However, in **A**, both atoms have complete octet, and the **presence of a triple bond** also makes **A** much more stable than **B** which has a double bond only.

(b) Organic cyanides are also known as nitriles. Compound **D** is an example of an organic cyanide.

Compound **D** is a fungicide used for the control of fungus that causes serious disease in rice fields. **D** is used as an equimolar mixture of two stereoisomers.

D has two Cl atoms and contains four other elements C, H, N and O only.

The infra-red and ^1H NMR of **D** are shown in Fig. 2.1 and Fig. 2.2 respectively.

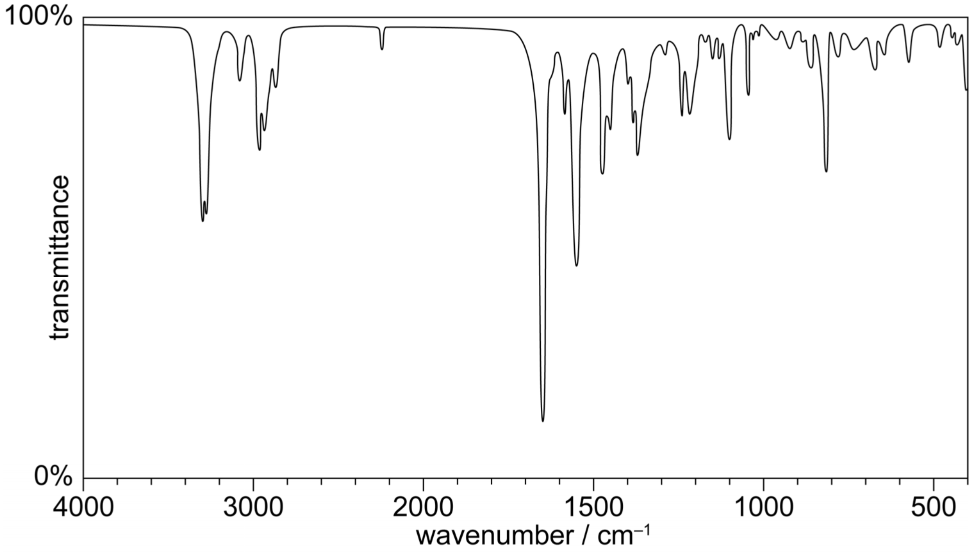


Fig. 2.1

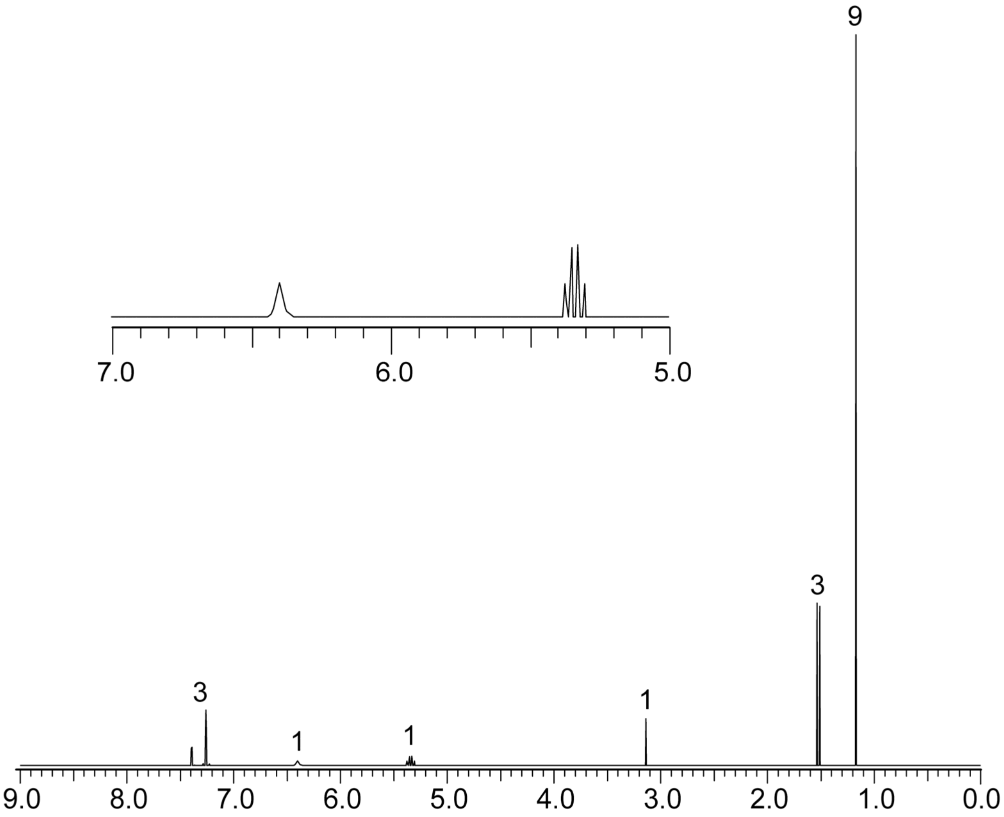


Fig. 2.2

In the NMR spectrum of **D**, the integration of each resonance is shown. The resonance at δ 6.4 disappears on the addition of D_2O.

The mass spectrum of **D** shows a molecular ion at *m*/*z* 312 and the following peaks.

m/*e*	relative abundance (%)
173	67.5
175	44.1
177	7.48
221	55.2
223	17.8
277	75
279	24.5
312	100
313	17
314	64.3
316	10.2

(i) Explain the relative intensities of the peak at *m*/*z* 312, 314 and 316 in the mass spectrum. [1]

(ii) Deduce the molecular formula and structural formula of compound **D**. Show your reasoning. [6]

(iii) Use your structure to identify the fragment ions at *m*/*z* 173, 221 and 277 in the mass spectrum of **D**. [2]

(i) The molecular ion must contain 2 C*l* atoms.

m/*z*	312	314	316
probability	$\frac{3}{4}\times\frac{3}{4}=\frac{9}{16}$	$2\times\frac{3}{4}\times\frac{1}{4}=\frac{6}{16}$	$\frac{1}{4}\times\frac{1}{4}=\frac{1}{16}$
relative intensity	9	6	1

(ii)

From the mass spectrum,

no. of C $=\left(\frac{100}{1.1}\right)\left(\frac{100}{17}\right)=15$, hence D has 15 carbon atoms

312 – (12 × 15) – (2 × 35) = 62 mass units for H + N + O.

Number of H (from NMR spectrum) = 18

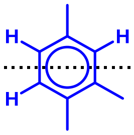
That leaves only 62 – 18 = 44 for N and O

Since we have at least 1 N and 1 O, 46 – 16 – 14 = 14, last atom is N.

D is thus $\mathbf{C_{15}H_{18}N_2OCl_2}$.

From the NMR spectra,

chemical shift, δ / ppm	no. of ^{1}H	multiplicity	no. of neighbouring H	structural fragment
1.2	9	singlet	0	$–C(CH_3)_3$
1.5	3	doublet	0	$–C\underline{H_3}$ next to –CH
3.1	1	singlet	0	isolated –CH
5.3	1	quartet	3	$–CH_3$ next to $–C\underline{H}$
6.4	1	broad singlet	–	–NH or –OH

chemical shift, δ / ppm	no. of ^{1}H	multiplicity	no. of neighbouring H	structural fragment
7.3	2	multiplet	–	
7.4	1	singlet	0	

From the IR spectra,

strong absorption ~1690 cm^{-1} ⇒ amide C=O stretch

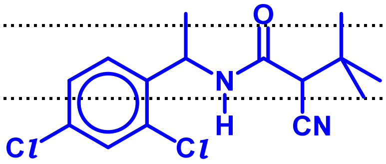
weak absorption at ~3300 cm^{-1} ⇒ amine/amide N–H stretch

seak absorption at ~2200 cm^{-1} ⇒ nitrile stretch

no strong peaks between 1000 cm^{-1}–1400 cm^{-1} ⇒ absence of alcohol

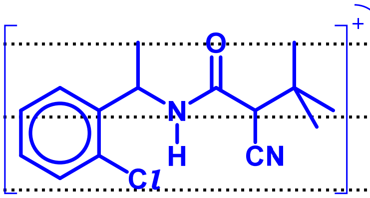
⇒ presence of amide in **D**

Considering that **D** must have –CN (nitrile) and at least 1 chiral carbon:

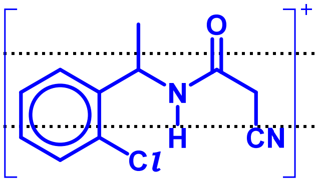


(iii)

m/*z* = 277

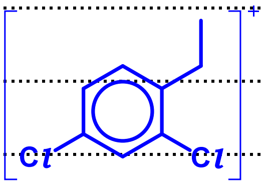


m/*z* = 221



characteristic 3 : 1 peak ratio of 1 Cl atom

m/*z* = 173



[Total: 11]

3 (a) Molecular orbital theory can be used to explain differences in certain physical properties such as bond energy and ionisation energy.

(i) Draw and use molecular orbital diagrams to predict how the bond order will change for the following processes. In each case, explain whether the neutral molecule or the cation has a stronger bond.

$$O_2 \rightarrow O_2^+ + e^-$$
$$F_2 \rightarrow F_2^+ + e^-$$

[4]

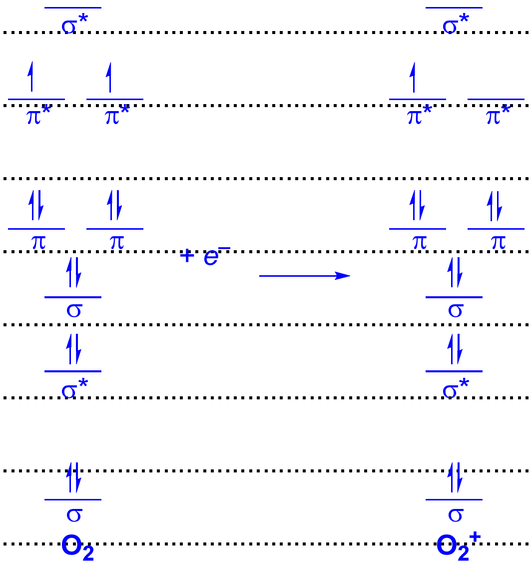
Some physical properties for these molecules are listed in Table 3.1.

Table 3.1

physical properties	process	values	
		O_2	F_2
bond energy / kJ mol^{-1}	$X_2(g) \rightarrow 2X(g)$	496	158
ionisation energy / kJ mol^{-1}	$X_2(g) \rightarrow X_2^+(g) + e^-$	1165	1515
bond length / nm		0.121	0.141

(ii) Using your answer in **3(a)(i)**, comment on the relative values of these three properties. [2]

(i) MO diagram for O_2 and O_2^+:

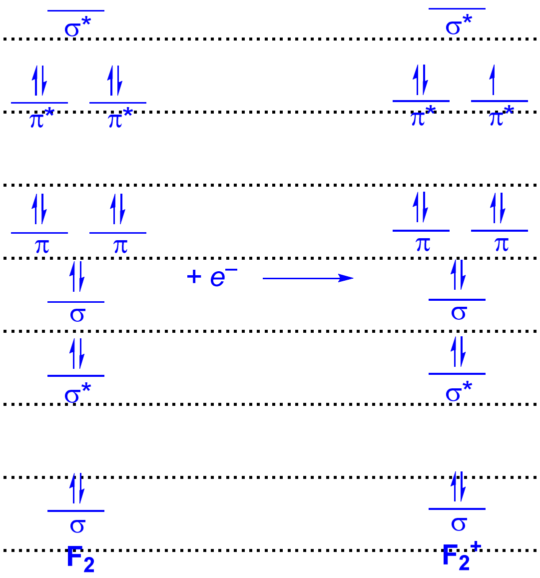


The electron will be removed from the π^* HOMO in O_2.

bond order in $O_2 = \frac{6-2}{2} = 2$; bond order in $O_2^+ = \frac{6-1}{2} = 2.5$

Hence the ion O_2^+ has the stronger bond.

MO diagram for F_2 and F_2^+:



The electron will be removed from the σ^* HOMO in F_2.

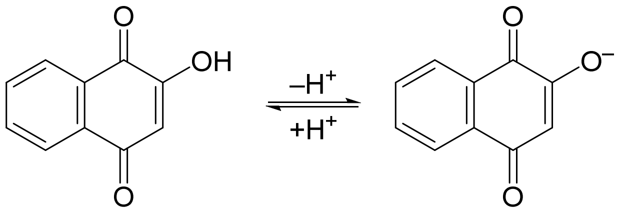
$$\text{bond order in } F_2 = \frac{6-4}{2} = 1 \text{ ; bond order in } F_2^+ = \frac{6-3}{2} = 1.5$$

Hence the ion F_2^+ has the stronger bond.

(ii) The **bond length and bond energy correlates with the bond order** of O_2 and F_2. **O=O with the shorter but stronger bond strength, and N≡N with the longer but weaker bond**.

Both electrons are found in the π^* orbital in O_2 and F_2. Since F is **more electronegative** than O, the orbitals and hence **the π^* orbital in F_2 will be lower in energy than that in O_2**, resulting in the higher ionisation energy of F_2 compared to O_2.

(b) Lawsone is a coloured dye found in Henna plants and is responsible for the characteristic red-brown colour in henna dyes. It exists in two different forms, **X** and **Y**.



X **Y**

X has a maximum absorption peak at approximately 334 nm and **Y** has a maximum absorption peak at approximately 453 nm in the UV spectra.

(i) Explain the principles of UV spectroscopy of organic molecules. [2]

(ii) State the two types of electronic transition that gives rise to the colour of **X**. [1]

(iii) Suggest explanations for the difference between the maximum absorption peaks for **X** and **Y**. [2]

(i) Organic molecules with **π bonds, conjugated π bond systems or contains atoms with lone pairs of electrons** can absorb energy in the UV region. The electrons in the **highest occupied molecular orbital (HOMO) can be excited to the lowest unoccupied molecular orbital (LUMO)**, where electronic **transitions such as $\pi \rightarrow \pi^*$, n $\rightarrow \pi^*$ and n $\rightarrow \sigma^*$ are allowed** for UV absorption.

(ii) **$\pi \rightarrow \pi^*$, n $\rightarrow \pi^*$**

(iii) For Y, the **lone pair of electrons on the O atom are more available for delocalisation into the π electron cloud ring, resulting in a greater extent of conjugation**. As such, **the energy gap between the π → π* will be smaller, leading to a lower energy and higher maximum absorbance wavelength**.

Question 3 continues on the next page

(c) The concentration of lawsone (M_r = 174) found in henna ink must meet a standard of not more than 10 g per cm^3. The concentration of lawsone can be determined quantitively by UV spe

(i) To determine the molar extinction coefficient of **X** at 334 nm, an experiment was conducted.

83.5 g of **X** was dissolved in 100 cm^3 of an acidic buffer solution to make a standard solution. Th

- 1 cm^3 of the standard solution was diluted with 99 cm^3 of deionised water.
- 1 cm^3 of the resulting solution was diluted with 99 cm^3 of deionised water.

1 cm^3 of the diluted solution was analysed using a UV spectrophotometer using a cell of pathlength of 1 cm. The absorbance at 334 nm was found to be 0.74.

Calculate the molar extinction coefficient of **X** at 334 nm. [2]

(ii) 1 cm^3 of the henna ink was diluted in 100 cm^3 of an acidic buffer solution. This diluted solution was found to have an absorbance of 0.87 at 334 nm with a cell of pathlength of 1 cm.

Using your answer in **(c)(i)**, calculate the concentration in g dm^{-3} in the sample.[2]

(iii) Suggest why the henna ink need to be diluted in an acidic buffer solution. [1]

(i) amt of lawsone in 100 cm^3 $= \dfrac{83.5}{174.15} = 4.795 \times 10^{-1}$ mol

$[\text{lawsone}]$ in standard solution $= \dfrac{4.795 \times 10^{-1}}{100/1000} = 4.795 \text{ mol dm}^{-3}$

$[\text{lawsone}]$ after 2$^{\text{nd}}$ dilution $= 4.795 \times 0.01 \times 0.01$

$= 4.795 \times 10^{-4} \text{ mol dm}^{-3}$

molar extinction coefficeint $= \dfrac{0.74}{(4.795 \times 10^{-4})(1)} = \underline{\mathbf{1543}}$

(ii) $[\text{lawsone}]$ in diluted solution $= \dfrac{0.42}{1543 \times 1} = 2.722 \times 10^{-4} \text{ mol dm}^{-3}$

$[\text{lawsone}]$ in henna ink $= (2.722 \times 10^{-4}) \times 100 = 2.722 \times 10^{-2} \text{ mol dm}^{-3}$

mass concentration of lawsone $= [\text{lawsone}] \times M = (2.722 \times 10^{-2}) \times 174.15$

$= \underline{\mathbf{4.74\ g\ dm^{-3}}}$

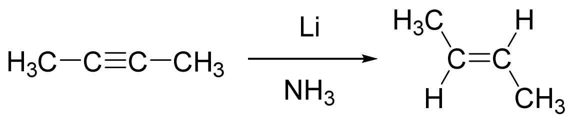
(iii) The acidic buffer solution allows **Lawsone to exist in the protonated form of X.** This ensures that the **quantitative analysis of Lawsone to be accurate.**

[Total: 16]

Question 4 starts on the next page

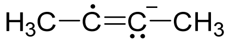
4 **(a)** This question is about reactions involving alkynes. An alkyne is a hydrocarbon that contains a carbon-carbon triple bond.

A method for reduction of alkynes to alkenes involve the use of lithium metal in liquid ammonia as so



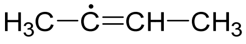
but-2-yne *trans*-but-2-ene

The first step of the mechanism involves Li metal that yields a carbanionic radical intermediate. This carbanionic radical, being a strong base, abstracts a proton from NH_3 to give a neutral radical intermediate. The structures of both intermediates are shown below.



$H_3C-\dot{C}=\underset{\cdot\cdot}{\overset{-}{C}}-CH_3$

carbanionic radical

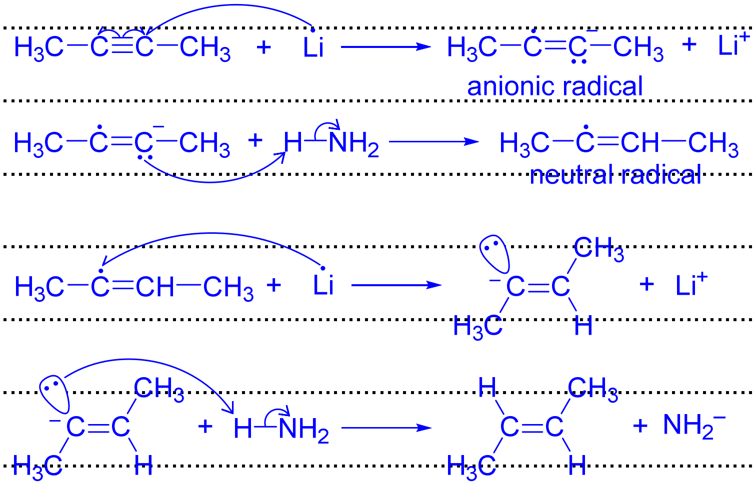


$H_3C-\dot{C}=CH-CH_3$

neutral radical

In subsequent step, a carbanion intermediate is formed stereoselectively before the final *trans* alkene product is formed.

With this given information, suggest the mechanism for reduction of but-2-yne giving *trans*-but-2-ene, showing clearly the structure of the carbanion intermediate, including its stereochemistry. [3]



(b) The most striking difference between alkynes and other hydrocarbons like alkanes and alkenes is that terminal alkynes are relatively acidic. Table 4.1 shows the pK_a of simple hydrocarbons.

Table 4.1

hydrocarbon	**pK_a**
$HC{\equiv}CH$	25
$CH_2{=}CH_2$	44
CH_3CH_3	60

(i) State the hybridisation of the carbon atoms of ethylene $HC{\equiv}CH$ and ethene, $CH_2{=}CH_2$. Hence, suggest why ethylene $HC{\equiv}CH$ is more acidic than ethene, $CH_2{=}CH_2$. [2]

When terminal alkynes such as ethyne is treated with a strong base, $NaNH_2$ in liquid NH_3, the termin

$$H{-}C{\equiv}C{-}H + NaNH_2 \longrightarrow \underset{\text{acetylide anion}}{H{-}C{\equiv}C^{-}Na^{+}} + NH_3$$

Fig. 4.1 shows two synthetic routes to the same product, compound **L**.

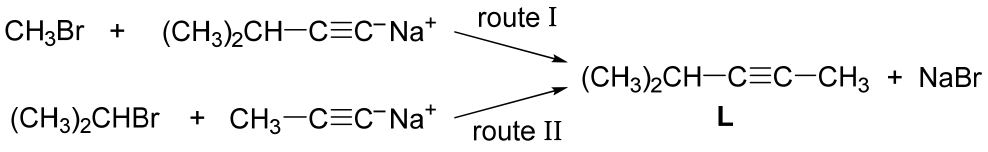
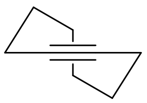


Fig. 4.1

(ii) Suggest the mechanism of the reaction from route I. [2]

(iii) With reference to **(b)(ii)**, explain why route II does not give satisfactory yield of **L**. Suggest the major products of route II. [2]

(iv) Suggest how you would prepare cyclooctyne starting from $HC{\equiv}CH$.



cyclooctyne

[1]

(i) The hybridisation of carbon atoms in ethyne ($HC{\equiv}CH$) is sp while that in ethene ($CH_2{=}CH_2$) is sp^2. **The s character of sp carbon (50% s character) is higher than sp^2 carbon (33.3% s character)** thus negative

(c) Alkynes can be synthesised by the dehydrohalogenation of vinylic halides, which may follow an E2 mechanism. To study the stereochemistry of this elimination, (*E*)- and (*Z*)-2-chlorobut-2-enedioic acid were treated separately with $NaNH_2$, and one of the isomer is found to react 50 times than the other.

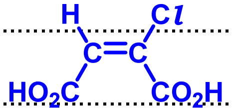
$$HO_2CHC{=}CClCO_2H \xrightarrow[\text{2. } H_3O^+]{\text{1. } NaNH_2} HO_2CC{\equiv}CCO_2H$$

2-chlorobut-2-enedioic acid

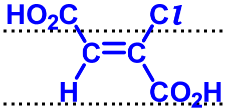
(i) Draw the (*E*)- and (*Z*)-isomers of 2-chlorobut-2-enedioic acid and assign the stereochemistry of each structure, explaining the reason for your choice. [2]

(ii) Assuming the elimination follows E2 mechanism, suggest and explain which stereoisomer reacts faster in this elimination. [1]

(i)



(*E*)



(*Z*)

In the **(*Z*)-isomer**, the higher priority groups on each of the double bond C, the **CO_2H group and Cl are on the same side of C=C double bond**, while for the **(*E*)-isomer**, the **CO_2H group and Cl are on opposite sides**.

(ii) The **(*Z*)-isomer react faster**. The hydrogen and chlorine are ***anti* with respect to each other in the (*Z*)-isomer** while they are *syn* in the (*E*)-isomer. **E2 mechanism** proceed more favourably when the **substituents to be eliminated are *anti*** to other each.

[Total: 13]

Section B starts on the next page

Section B

Answer **two** questions from this section.

5 **(a)** **(i)** Explain the origin of infra-red (IR) absorptions of simple molecules. [2]

(ii) Predict the number of absorptions in the IR spectrum of NO and NO_2, and describe the vibrations that give rise to these absorptions. [2]

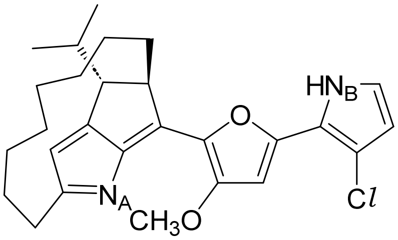
(i) **Different modes of vibrations** in a molecule give rise to **different vibrational energy levels**, such as stretching and bending. Absorption of radiation in the IR region occurs when **frequency of incident radiation equals that of the difference between vibrational energy levels**.

For a vibrational mode to be IR active, there must be a **net change in dipole moment of molecule when the vibration occurs**. Bond strength affects the frequency of IR radiation absorbed, and since each functional group possess certain bonds, they show absorption at characteristic wavenumbers in the IR spectra.

(ii) NO: **1** absorption band (NO **stretching**)

NO_2: **3** absorption bands (**symmetrical stretch, asymmetrical stretch, bending**)

(b) Roseophilin is an antibiotic that is shown to have antitumor activity.



roseophilin

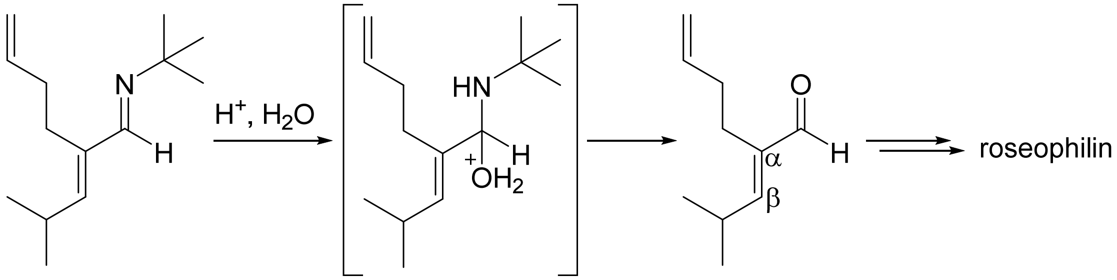
The two nitrogen atoms, N_A and N_B, have the same hybridisation.

Explain which of the two nitrogen atoms, N_A or N_B, in roseophilin is a weaker base, and why both are weaker bases than ammonia. [2]

The **lone pair of electrons on N_B are part of the delocalised π electron cloud in the 5-membered ring**, thus making it less available for donation, while **the lone pair of electrons on N_A are not delocalised**, and hence would be more available for donation to a proton.

Both N in roseophilin is **sp^2 hybridised**, while the N in NH_3 is **sp^3 hybridised**. As an **sp^2 hybrid orbital has larger % s character than a sp^3 hybrid orbital, the lone pair of electrons on both N in roseophilin will be closer to the nucleus and more strongly attracted to the nucleus**, rendering it less available for donation to a H^+ compared to the lone pair on N in NH_3, and thus less basic.

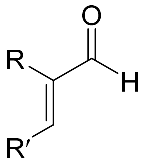
(c) Part of the synthesis of roseophilin is shown.



W **X** **Y**

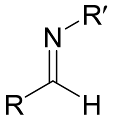
(i) The C=O stretch of aliphatic aldehydes occur at about 1730 cm^{-1}.

Explain, with the aid of suitable resonance structures, how the frequency of the C=O stretch in the α,β-unsaturated aldehyde in **Y** would compare with that of aliphatic aldehydes.

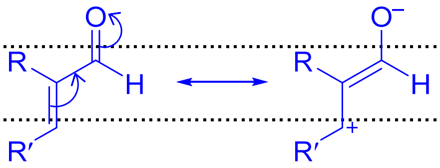
You may use  to represent the structure of the α,β-unsaturated aldehyde. [2]

(ii) The imine (C=N functional group) in **W** undergoes acid-catalysed hydrolysis readily to form the aldehyde in **Y** *via* the formation of intermediate **X**.

Suggest a mechanism for the acid-catalysed hydrolysis to convert **W** to **Y**.

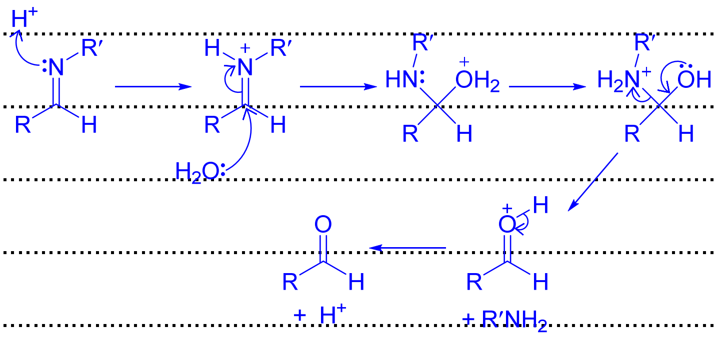
You may use  to represent the imine in **W**. [2]

(i)



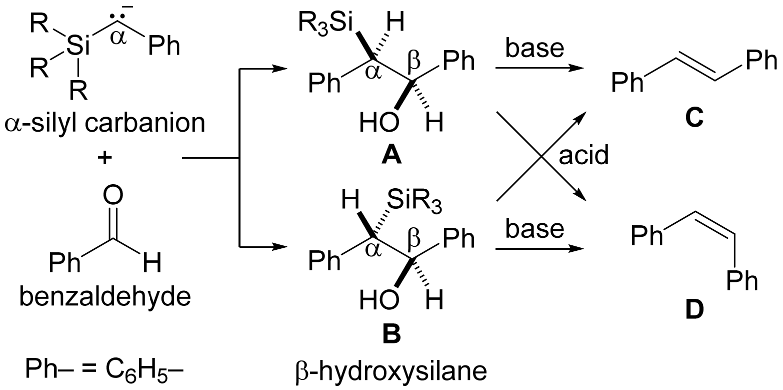
From the resonance structure, C=O bond length is increased/gains more C–O single bond character. The C=O stretch thus occurs at lower energy, corresponding to a frequency lower than 1700 cm^{-1}.

(ii)



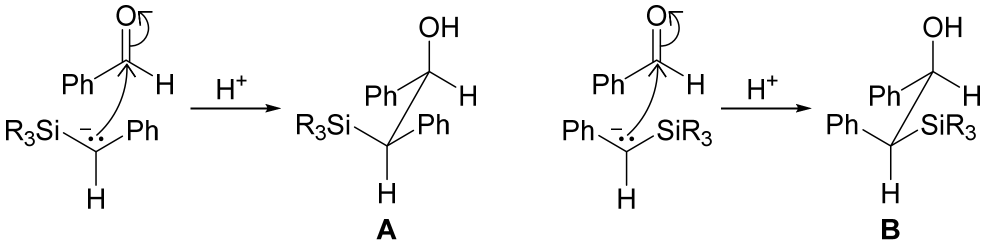
....

(d) The alkene on the α-carbon of the imine in **W** may be formed from reaction of α-silyl carbanions with suitable carbonyl compounds to form diastereomeric β-hydroxysilane which may be isolated. Depending on whether an acid or a base is added, the β-hydroxysilane can undergo stereospecific elimination to produce either the (*E*)- or (*Z*)- alkene. This reaction is known as the Peterson reaction.



(i) Suggest reagents and conditions for the synthesis of benzaldehyde from benzene, showing all ir

The first step of the Peterson reaction involves the addition of the α-silyl carbanion to benzaldehyde. The reaction may proceed in two ways as shown to give diastereomeric β-hydroxysilane **A** and **B**.



As the size of the alkyl group (R) of the α-silyl carbanion increases, it was found that the formation of diastereomer **B** was favoured.

(ii) Explain why small alkyl group (R) of the α-silyl carbanion favours the formation of **A**, but the selectivity shifts towards the formation of diastereomer **B** when the size of the alkyl chain in the silyl group increases. [2]

The alkenes **C** and **D** are both formed via E2 elimination of β-hydroxysilane.

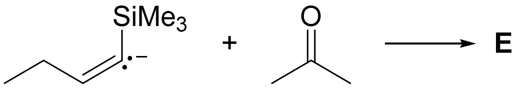
(iii) Draw the mechanism for the acid-catalysed conversion of **B** to **C** in the presence of water. [1]

(iv) Suggest why the acid-catalysed elimination reaction takes place slower for **A** compared to **B**. [1]

(v) In the base-catalysed elimination, the strong base deprotonates the alcohol to form an alkoxide ion. The alkoxide ion then rapidly reacts with the silane to form a strong Si–O bond. Elimination then occurs to form the alkene.

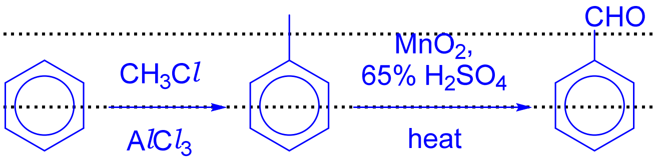
Suggest the mechanism for the base-catalysed conversion of **B** to **D** using hydride, H^-, as the base. Show clearly the stereochemistry of the reaction that is occurring. [2]

(vi) Predict the structure of the product **E** formed when the following compounds undergo the Peterson reaction.



[1]

(i)

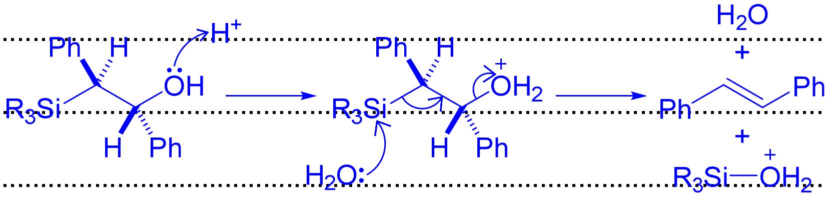


The reaction can actually be done in a single step using CO, HCl, $AlCl_3$.

(ii) When the size of the alkyl group is small, the **steric repulsion between the two Ph groups would be greater**, and hence the **two Ph groups would adopt an *anti*-configuration**, favouring the formation of **A**.

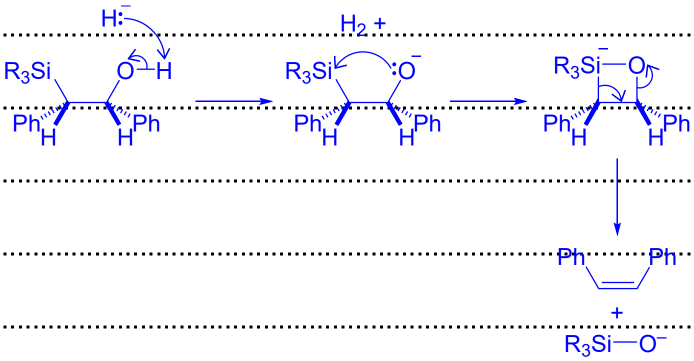
As the size of the alkyl chain increases, the silyl group will **prefer to adopt an *anti*-configuration to the Ph ring in the transition state instead** so as to **minimise repulsion between the bulky groups** present.

(iii)

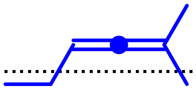


(iv) A likely **exists in a conformation where the two bulky Ph rings exist anti to one another**. However, for E2 to occur, **the -OH and -SiR$_3$ groups need to be anti-periplanar to each other**. The E2 reaction of **A** is thus **slower as the bonds must rotate such that the Ph groups are gauche (less stable conformation) before E2 can occur**.

(v)



(vi)



[Total: 20]

Question 6 starts on the next page

6 This question covers the kinetics mechanistic studies of nucleophilic substitution reactions.

(a) The hydrolysis of 2-chloro-2-methylpropane can take place with the following equation.

$$(CH_3)_3C\ell + H_2O \rightarrow (CH_3)_3COH + HC\ell$$

The reaction was found to follow overall first order kinetics. The following two mechanisms proposed are consistent with this finding.

mechanism 1

$$(CH_3)_3CC\ell + H_2O \xrightarrow{k} (CH_3)_3COH + HC\ell \qquad \text{rate determining step}$$

mechanism 2

$$(CH_3)_3CC\ell \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3C^+ + C\ell^- \qquad k_{-1} \,\square\, k_1$$

$$(CH_3)_3C^+ + H_2O \xrightarrow{k_2} (CH_3)_3COH + H^+ \qquad \text{fast reaction } (k_2 \,\square\, k_1)$$

(i) Explain why both mechanisms show overall first order kinetics. [4]

(ii) The second mechanism predicts that the rate decreases if $[C\ell^-]$ is increased. Explain qualitatively why the addition of $C\ell^-$ ions slow down the reaction. [2]

(iii) Draw an energy profile diagram for mechanism 2 when k_2 is of similar magnitude to k_{-1}. The diagram should show:

- the reactants, products and intermediates
- the three activation energies, labelled $E_a(k_1)$, $E_a(k_{-1})$ and $E_a(k_2)$ [3]

(iv) For the hydrolysis of 2-bromo-2-methylpropane, it is expected that the rate will be different.

Apart from bond strength considerations, predict and explain how the rate of hydrolysis of 2-bromo-2-methylpropane with 2-chloro-2-methylpropane will differ.[1]

(i) For mechanism 1:

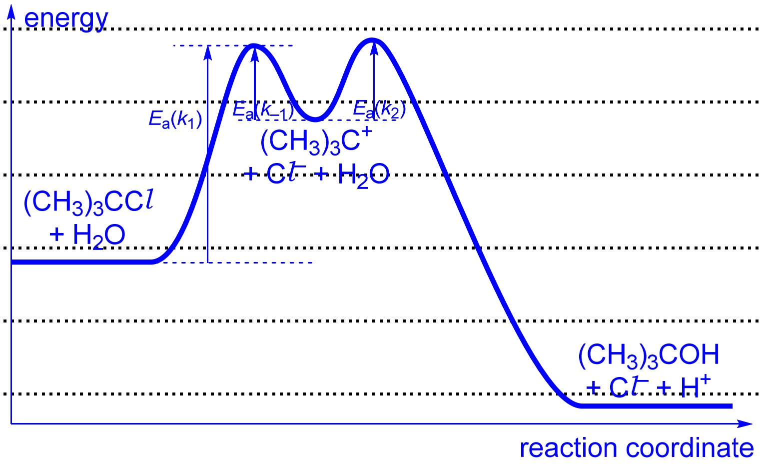
Based on the rate determining step, the **rate equation is rate = $k[(CH_3)_3C\ell][H_2O]$**. Since **H_2O is a solvent, thus its concentration is considered to be constant**, the overall rate equation can be written as **rate = $k'[(CH_3)_3C\ell]$, where $k' = k[H_2O]$, and is pseudo-first order**.

For mechanism 2:

The first slow equilibrium step, has a **slow forward reaction, which is considered the rate determining step**. The rate equation for this step is **rate = k_1[$(CH_3)_3CCl$]**. As the **overall reaction is dependent on the slowest elementary step**, hence the overall rate equation is **rate = k_1[$(CH_3)_3CCl$], and is overall first order**.

(ii) When [Cl^-] increases, **the chloride ions can act as a nucleophile, reacting with the carbocation intermediate to reform the reactant. This reduces the amount of carbocation intermediate that can react with water to form the alcohol in the second step, hence slowing down the reaction**.

(iii)



(iv) By considering the **rate determining step**, it involves the halide ion leaving. Br^- is a **better leaving group** than Cl^- as it is **a more stable conjugate base**. Hence, the **rate of reaction will increase.**

....

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(b) The inversion of S_N2 mechanism is also known as the Walden inversion. This was discovered via a mechanistic study involving the Walden cycle, which shows one enantiomer being converted into the other enantiomer and back again.

The classic Walden cycle is shown in Fig. 6.1.

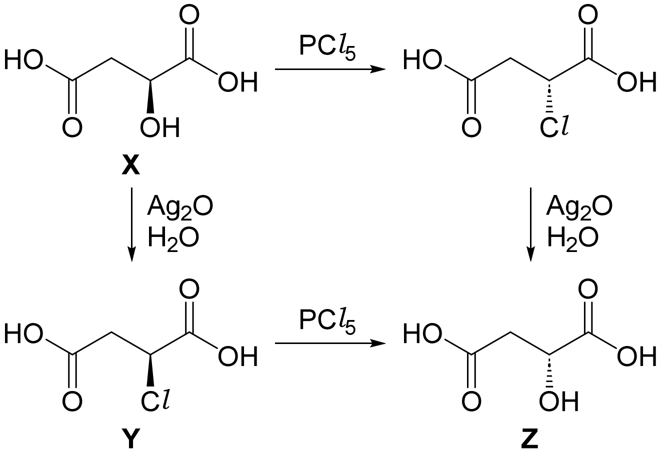


Fig. 6.1

The inversion of the stereochemistry was determined using the known specific rotation of **X** and **Z**. The specific rotation of **X** is –2.3°.

(i) Assign the stereochemistry (*R* or *S*) at the chiral carbon in **X**, and explain your answer. [1]

(ii) An unknown composition mixture of **X** and **Z** was analysed using a polarimeter. The observed rotation of the solution was +0.68°.

Determine the percentage composition of **X** and **Z** in the mixture. State any assumptions that yo

It is found that the reaction of **Y** to form **X** follows 2 inversions of configurations, leading to a retention of configuration at the chiral carbon. The mechanism is as described below:

1. Deprotonation of the carboxylic acid by the Ag_2O base. You may assume it provides the hydroxide ion, OH^-.
2. Attack of the chiral centre by the resulting carboxylate anion, forming a four-membered ring.
3. Attack of the chiral centre by a hydroxide ion, leading to the ring opening.

(iii) Describe the mechanism for this reaction. Show all relevant lone pairs and charges and indicate the movement of electron pairs with curly arrows. Use bold and hashed wedges to describe the stereochemistry when relevant. [3]

(i) Compound **X**: ***S***

In compound **X**, the highest priority group (–OH), the 2nd priority group (–CO_2H) and the 3rd priority group (CH_2) are arranged in an anti-clockwise direction. Hence, the configuration is **S** for compound X.

(ii) Assume that the observed rotation is the **sum of the optical rotations of each compound**.

Let *x* be the mole fraction of **X**.

$+0.68^\circ = (x)(-2.3^\circ) + (1 - x)(+2.3^\circ)$

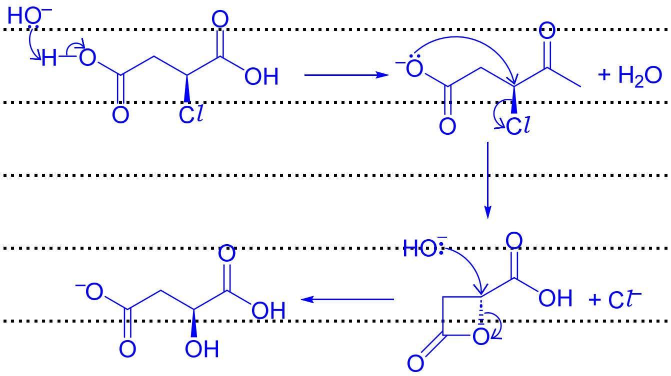
$+0.68^\circ = -4.6x^\circ + 2.3^\circ$

$4.6x^\circ = 1.62^\circ$

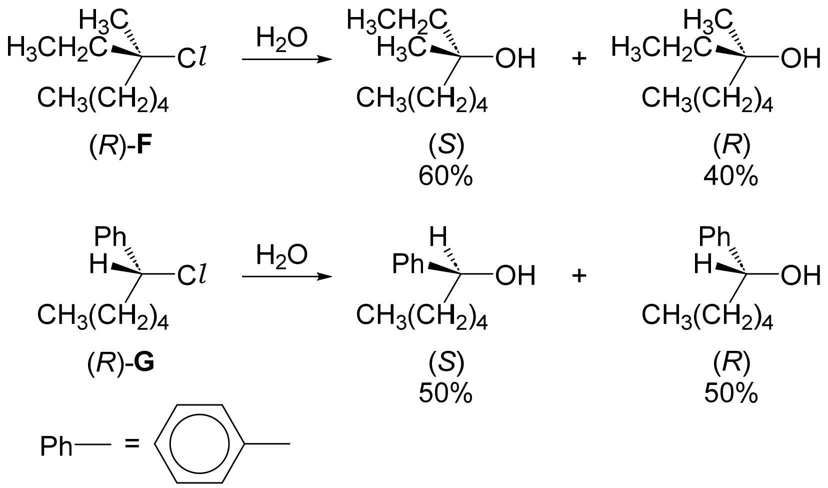
$x = 0.352$

The mixture consists of **35.2% X** and **64.8% Y**

(iii)



(c) The following hydrolysis reactions involve two enantiomerically pure chloroalkanes undergoing unimolecular nucleophilic substitution.



The reaction with compound **F** leads to incomplete racemisation while the reaction with compound **G** leads to complete racemisation.

By considering the stability of the carbocation intermediate, account for the differences the reactions involving compound **F** and **G**. [4]

For Compound **F**, the **carbocation intermediate formed is unstable and highly reactive**. It reacts very quickly with H_2O, such that **it has not completely separated from the chloride anion, leading to an ion pair**. The **ion pair that partially protects one side of the carboncation intermediate from nucleophilic attack**, leading **to the nucleophile preferentially attacking from the side that lies opposite of the chloride anion**, leading to incomplete racemisation.

For Compound **G**, **the carbocation intermediate formed is stabilised by the phenyl ring via resonance effect, which disperses the positive charge to a larger extent**. This allows for the **chloride anion to leave the carbocation intermediate and is solvent separated**. Hence, **the nucleophile can attack from both sides of the carbocation intermediate**, leading to complete racemisation.

....

[Total: 20]

7 **(a)** Styrene oxide can be hydrolysed into styrene glycol in a wide range of pH. Interest in mechanistic understanding of this process is attributed to possible carcinogenic metabolites of these compounds.

A study of hydrolysis of styrene oxide and its 4-substituted derivatives under acidic conditions, shown in Fig. 7.1, has been carried. The experimental results are as follows.

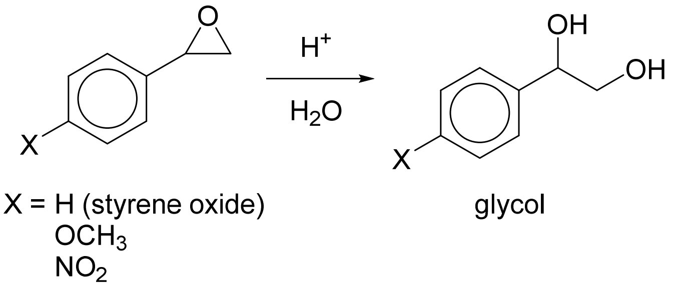


Fig. 7.1

The observed rate constant, k_{obs}, for the hydrolysis of 4-substituted styrene oxides to their corresponding glycols is given by equation 1.

equation 1 $k_{obs} = k_o + k_H[H^+]$

where k_o = rate constant for non-catalysed spontaneous reaction
k_H = rate constant for acid-catalysed reaction

The effects of the nature of the 4-substituent on the acid-catalysed rate constants, k_H, are shown in Table 7.1.

Table 7.1

X	k_H / mol^{-1} dm^3 s^{-1}
OCH_3 (methoxy)	1.10×10^4
H	26.6
NO_2 (nitro)	3.41×10^{-3}

The acidic hydrolysis of styrene oxide in $H_2{}^{18}O$ yields styrene glycol in which all the ^{18}O is incorporated on the α-carbon as shown in Fig. 7.2. This implies that nucleophilic attack of water occurs at the α-carbon.

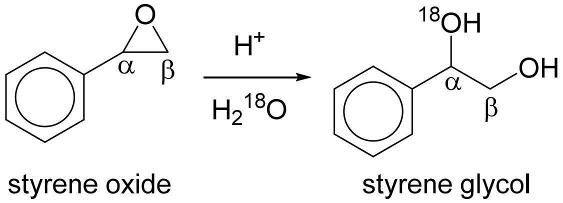


Fig. 7.2

It is also found that hydrolysis of (*R*)-(+)-styrene oxide yields a racemic mixture of styrene glycols, whereas acid methanolysis yields a product with 89% inversion of configuration at the α-carbon, as shown in Fig. 7.3.

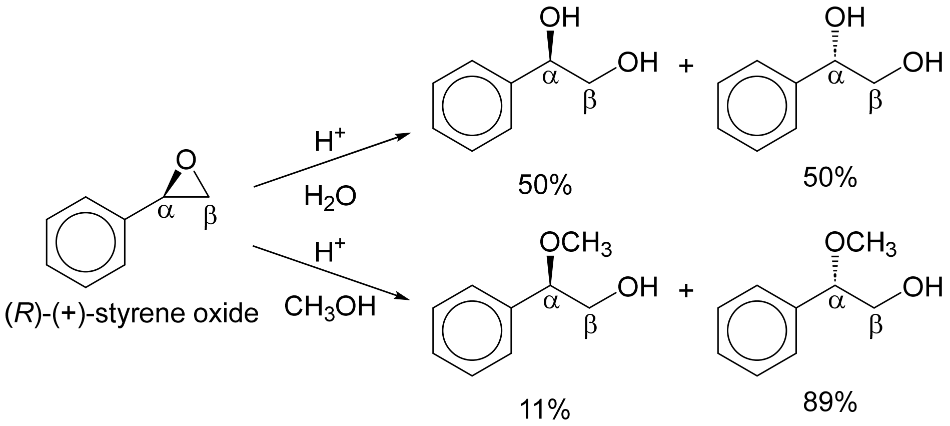


Fig. 7.3

(i) Suggest why nucleophilic attack of water solely at the α-carbon rules out a S_N2 mechanism for the acid hydrolysis of styrene oxide. [1]

(ii) By considering the given information, suggest why a carbocation intermediate may be involved for hydrolysis in acidic medium. [1]

(iii) By considering Hammond's postulate and the stability of the carbocation intermediate involved for hydrolysis in acidic medium, explain the effects of the 4-methoxy and 4-nitro substituents on k_H in Table 7.1.

You should explain your answer fully using appropriate diagrams showing how the methoxy and nitro groups affect the stability of the carbocation intermediate. [3]

(iv) The overall order of reaction for hydrolysis of styrene oxide with $H_2{}^{18}O$ in acidic medium is 2.

Based on the evidence given, draw the mechanism of this reaction, indicating the slow step. You mean use Ph to denote the phenyl group in your answer. [3]

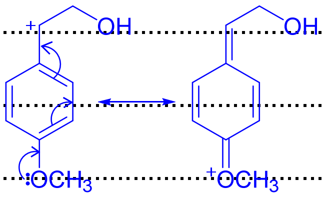
(v) Suggest a possible reason why the use of methanol in acid methanolysis of (*R*)-(+)-styrene oxide yields a product with 89% inversion of configuration at the α-carbon, rather than racemisation in acidic hydrolysis of (*R*)-(+)-styrene oxide.[2]

(i) A S_N2 mechanism will favour attack at the **less hindered** primary β-carbon instead of the secondary α-carbon.

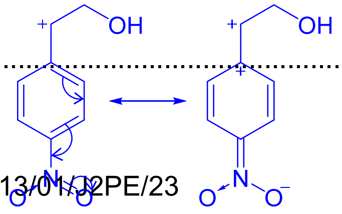
(ii) The **racemic products** formed from **(*R*)-(+)-styrene oxide** is resulted from **equal chance of nucleophilic attack on either face of the planar carbocation intermediate.**

(iii) Formation of carbocation intermediate involves bond breaking only and hence is endothermic. By Hammond's postulate, the **structure of the transition state ensembles that of the carbocation**. Hence, the **more stable carbocation** is **lower in energy**, leading to a **lower activation energy**.

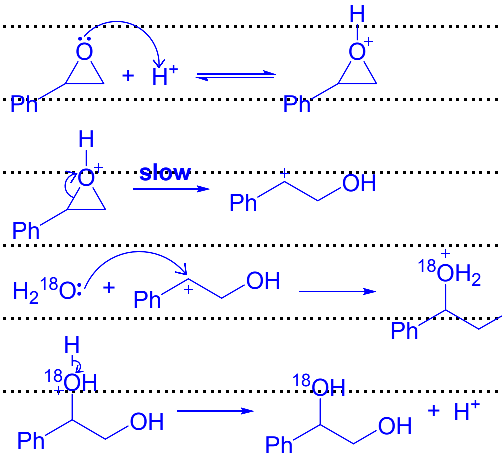
The electron-donating methoxy group disperse the positive charge of the carbocation intermediate compared to hydrogen, stabilising the carbocation, thus lowering the activation energy, increasing k_H.



The **electron-withdrawing nitro group intensifies the positive charge of the carbocation intermediate compared to hydrogen**, destabilisng the carbocation, thus raising the activation energy, decreasing k_H.



(iv)



(v) **CH_3OH is less polar** than water.

The –OH leaving group does not leave the resulting carbocation fully, substantially blocking one face of the carbocation (similar to ion-pair). The **opposite face is more accessible** to the methanol nucleophile, leading to **inversion**.

or

CH_3OH is stronger nucleophile than water.

A **competing S_N2 reaction could have occurred at the α-carbon before carbocation intermediate was formed, resulting in inversion**.

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Question 7 continues on the next page

(b) Trimethylaluminium, TMA, is one of the simplest examples of an organoaluminium compound. Despite its name it has the formula $Al_2(CH_3)_6$, as it exists as a dimer, like Al_2Cl_6, where the aluminium centres are tetrahedral.

(i) Explain why Al_2Cl_6 exist as a dimer and draw the structure of the dimer, showing the stereochemistry. [2]

(ii) With reference to the structure of Al_2Cl_6, explain why dimer, $Al_2(CH_3)_6$ is not expected. [1]

TMA is a source of methyl nucleophiles and reacts with epoxides in ring-opening reactions similar to the hydrolysis reaction in **(a)**.

(iii) Suggest why TMA is a source of methyl nucleophiles. [1]

However, TMA is a poor nucleophile. In the reaction with epoxides, the epoxide first reacts with TMA to give an adduct, which helps to render both the epoxide as well as TMA more reactive towards subsequent ring-opening S_N2 attack, as shown in Fig. 7.4.

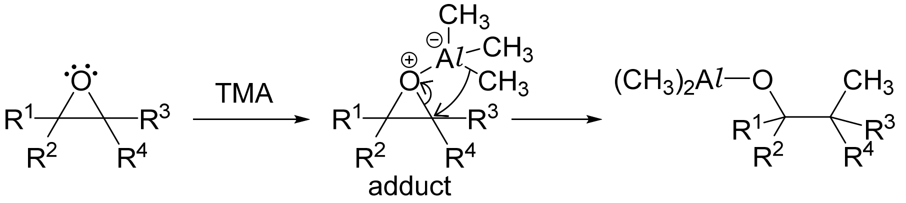


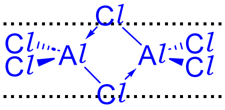
Fig. 7.4

(iv) Suggest how formation of the adduct helps to render both the epoxide as well as TMA more reactive towards subsequent nucleophilic attack in Fig. 7.4 [2]

The reaction rate is sensitive to type of solvent being used. The use of dichloromethane, CH_2Cl_2, solvent is optimal while the use of hexane gave low yield of the ring-opened products.

(v) Suggest why dichloromethane solvent gives better yield of the desired products than hexane solvent. [1]

(i) The aluminium in the monomer, $AlCl_3$, has **6 valence electrons** and is **electron-deficient**. Formation of the dimer helps Al **achieve an octet**.



(ii) The **chlorine atoms** in **$AlCl_3$** possess **lone pairs of electrons** which can be **donated** to the electron-deficient Al of another monomer to form the dimer. However, the **methyl groups** in $Al(CH_3)_3$ **do not possess any lone pair** for donation.

(iii) As carbon is **more electronegative** than aluminium, the **H_3C–Al bond** is polarised in such a way that the carbon carries the **partial negative (δ–) charge**, and thus can **donate the C–Al bond pair** serving as a source of methyl nucleophiles.

(iv) Formation of the adduct imparts a **positive charge** on the epoxide **oxygen**, making the oxygen a **better acceptor** of the **C–O bond pair** during ring-opening.

Formation of the adduct imparts a **negative charge** on the aluminium, making the **carbon a better donor** of the **Al–C bond pair** during nucleophilic attack, as the resulting aluminium in the product will be neutral.

(v) The **more polar dichloromethane solvent is better at stabilising the ionic adduct by forming ion-dipole interactions than the non-polar hexane solvent that cannot form favourable interactions.**

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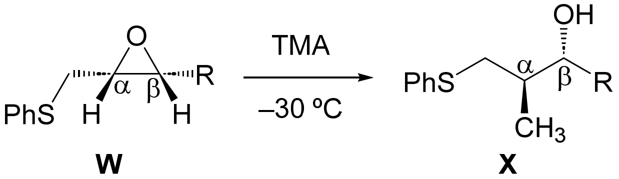
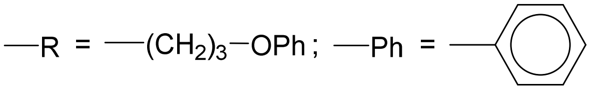
(c) With chiral epoxy sulfide **W**, TMA reacts both regioselectively and stereospecifically as shown in reaction 1, to give alcohol **X**, after aqueous workup.

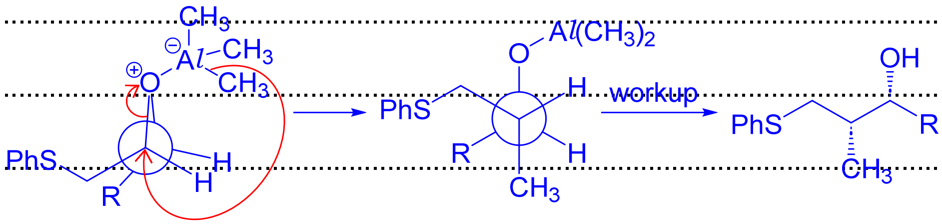
reaction 1





However, **X** is not the expected product from a direct S_N2 attack of the methyl nucleophile at the α-carbon, similar to that in Fig. 7.4. Rather, **X** is the result of neighbouring group participation by the –SPh group in **W**.

With the aid of an appropriate Newman projection of the adduct between epoxy sulfide **W** and TMA, similar to that in Fig. 7.4, draw the mechanism for a direct S_N2 ring-opening of **W** by TMA, showing the stereochemistry of the expected alcohol product after workup. [3]



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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2023
General Certificate of Education Advanced Level
Higher 3

CHEMISTRY

9813/01

Paper 1
INSERT

06 September 2023

2 hours 30 minutes

INSTRUCTIONS

This insert contains information for Question 1. **Do not write your answers on the insert**.

This document consists of 4 printed pages.

Information for Question 1

To honour the Paris Agreement, a global net zero greenhouse gasses (GHG) emission needs to be realised by the end of this century. Among all GHG's, CO_2(g) is accepted to be the main anthropogenic (that is, resulting from resulting from the influence of human beings on nature) control knob on the climate and has been the focus of many studies. The concentration of CO_2 in the atmosphere is approximately 278 ppm during the 10,000 years up to 1750, 300 ppm in the 1910s, 350 ppm in the late 1980s, and 418.6 ppm in 2022.

The concentration of CO_2 in the atmosphere is commonly reported as a mole fraction in dry air, expressed in ppm.

$$\text{concentration of } CO_2 = \frac{\text{amount of } CO_2}{\text{amount of air}} \times 10^6 \text{ ppm}$$

The following abstract is adapted from the work of R. Sharifian et al., *Energy Environ. Sci.*, 2021, 14, 781.

Carbon cycle (Data extracted from P Friedlingstein et al., *Earth Syst. Sci. Data*, 2022, 14, 4811)

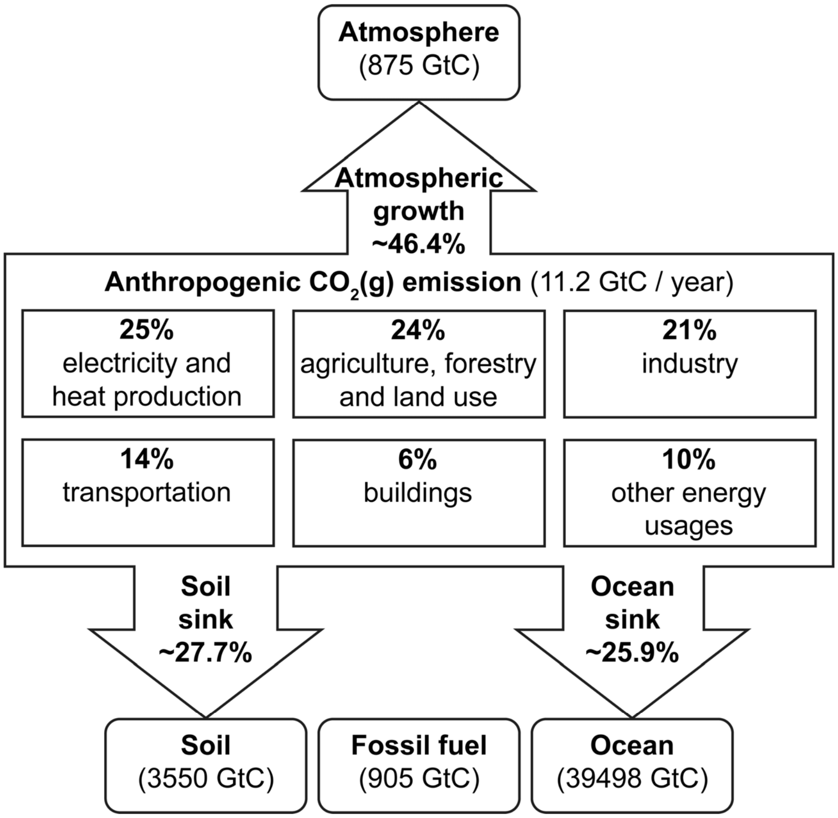


Fig. 1.1

A schematic of the global carbon cycle is shown in Fig. 1.1. The total carbon reserve on Earth as of 2022, spread across the atmosphere, the soil, the ocean and as fossil fuel, is shown in gigatones (10^{12} kg) of carbon (GtC). The global anthropogenic GHG emissions in CO_2(g) by different economic sectors is also shown. Approximately 50% of the anthropogenic CO_2 released into the atmosphere remains in the atmosphere, while about 25% is absorbed by the soil (soil sink), and the other 25% is absorbed into the ocean (ocean sink).

To achieve a net zero emission, reducing the total CO_2 emission obtains most impact in the short term. However, in the long run, in addition to emission reduction, CO_2 capture and utilisation is required.

CO_2 capture

According to Henry's Law, for the dissolution of CO_2(g) in water,

equilibrium 1 $\qquad CO_2(g) \rightleftharpoons CO_2(aq)$

the mole fraction of CO_2 in water, χ_{CO_2}, is proportional to its partial pressure in the gas phase, p_{CO_2}:

$$p_{CO_2} = K_H \chi_{CO_2}$$

where $\chi_{CO_2} = \dfrac{\text{amount of } CO_2}{\text{amount of } CO_2 + \text{amount of } H_2O}$, and

K_H = Henry's Law constant for CO_2

Like other equilibrium constants, K_H is temperature dependent, and the K_H for CO_2, in 10^6 Pa, is related to the thermodynamic temperature, T, in Kelvin, by the following equation:

$$\ln\left(K_H/10^6\ \text{Pa}\right) = -6.8346 + \frac{1.2817\times10^4}{T} - \frac{3.7668\times10^6}{T^2} + \frac{2.997\times10^8}{T^3}$$

CO_2 equilibrium

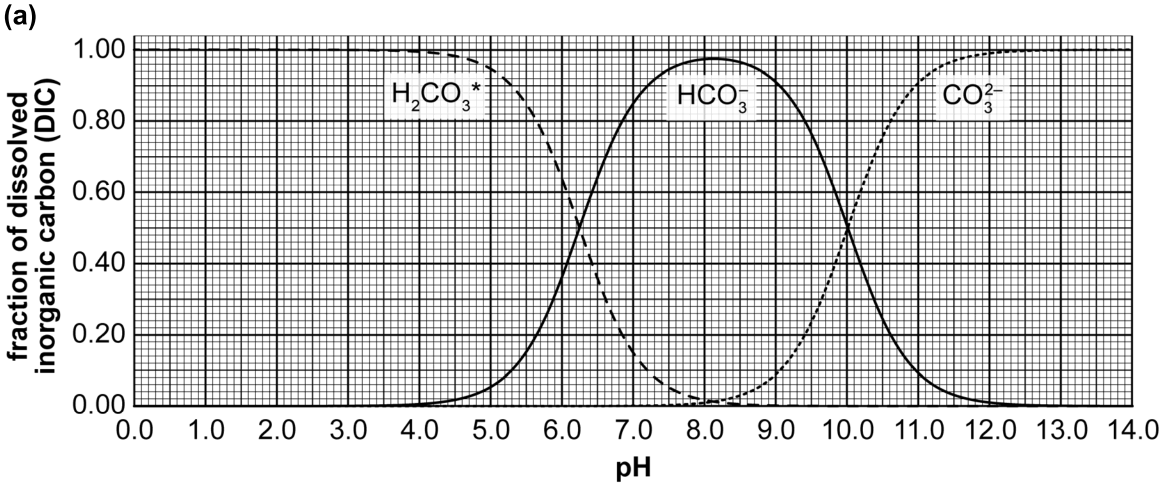
When CO_2(g) is dissolved in water, it can exist in a variety of forms, namely, CO_2(aq), H_2CO_3(aq), HCO_3^-(aq) and CO_3^{2-}(aq), depending on pH as shown in Fig. 1.2(a) and (b).

The sum of the concentration of all these carbonic species is known as the dissolved inorganic carbon, DIC:

$$\text{DIC} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

where $H_2CO_3^* = H_2CO_3(aq) + CO_2(aq)$.

At elevated alkalinity, the total solubility of CO_2(g), and hence DIC increases, while at elevated acidity, total solubility of CO_2(g), and hence DIC decreases.



(b) $$CO_2\,(aq) \xrightleftharpoons{H_2O} H_2CO_3\,(aq) \xrightleftharpoons[+H^+]{-H^+} HCO_3^-\,(aq) \xrightleftharpoons[+H^+]{-H^+} CO_3^{2-}\,(aq)$$

Fig. 1.2

Electrochemical pH-swing concepts

A wide variety of efforts to electrochemically capture CO_2 has been demonstrate in the past 50 years, with an intensification of research activities in the last two decades. One area of focus are electrochemical methods that use a pH-swing concept, as shown in Fig. 1.2(a) and 1.2(b). The swing refers to (electrochemically) shifting the pH of a working fluid (continuously) between basic and acidic pH to influence the CO_2 equilibrium to capture and recover CO_2.

Electrolysis of water can enable the pH-swing in the vicinity of two electrodes as shown in Fig. 1.3.

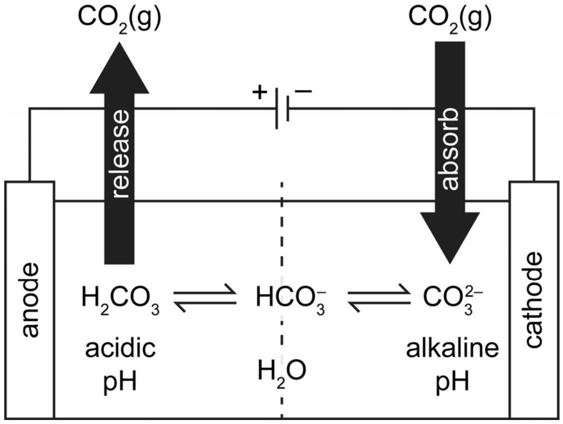


Fig. 1.3