IDK Junior College

CANDIDATE NAME

**CHEMISTRY SOLUTIONS**

**9476/02** **2 hours**

**Additional Material(s):** None

**READ THE FOLLOWING FIRST**

I do hope you have enjoyed/learnt something from this paper. It is meant to be a tad unconventional and unusual, do take heart in having tried your very best!

For organic structures, it will be penalised on the front page under structures if bonds are not bonded to the correct atom, e.g. C–HO, C–$H_2$N et cetera.

This is the first paper I have ever made, so any feedback/inquiries will be greatly appreciated! Despite best attempts to ensure accuracy, some mistakes may arise and if so, do email ian321714@gmail.com.

In general, answers are written in blue with their marks denoted next to them. Diagrams are in black because my software does not support other colours unfortunately :(

Information written in red are deductions/potential pitfalls that you must look out for, or just general helpful tips.

This document consists of **16** pages

Answer **all** questions

**1** Squaric acid is a dibasic organic acid. Fig. 1.1. shows the skeletal formula of squaric acid.

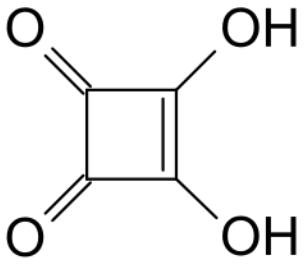



**Fig. 1.1**

**(a)** State the IUPAC name of this compound. You are told that priority goes to the carbonyl groups. (suffix) [2]

3,4-dihydroxycyclobut-3-en(e)-1,2-dione

- 1 mark for correct numbering
- 1 mark for correct name
- The (e) is optional.

**(b)** Fig. 1.2 shows the delocalisation of the divalent squarate anion. Draw, on Fig 1.2, curly arrows and lone pairs to show how this resonance stabilisation is achieved, from left to right. [1]

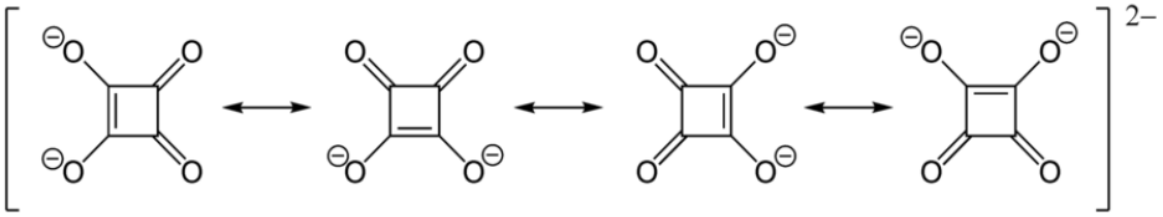


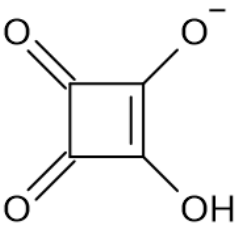

**Fig. 1.2**

**(c)** Hence, suggest why the divalent squarate anion is a perfect square. [1]

The electrons are delocalised equally across the entire molecule, and so the electron density is equally distributed, so the bond lengths of the bonds are equal, resulting in a perfect square.

- 1 mark for both parts

**(d)** Given that the 1st pKa of squaric acid is 1.5, draw the predominant species present at pH 3 [1]




[1] For correct species drawn (only 1 H is deprotonated) **with** a negative charge

**(e)** You are given squaric acid, ethanoic acid and ethanol at equal concentrations. Describe their relative acidities and explain. [3]

From most acidic to least acidic: squaric acid, ethanoic acid, ethanol. Squaric acid is most acidic due to the negative charge on the oxygen atoms on the divalent squarate anion/conjugate base (if discussion is on squaric acid instead of the c.base, no marks awarded) being able to be delocalised throughout the entire molecule, dispersing the negative charge to the greatest extent compared to the other two molecules. (1 mark for describing squaric acid)

For ethanoic acid, the negative charge on the ethanoate anion (if discussion is on ethanoic acid here, no marks awarded) is delocalised over two equally electronegative atoms but not the entire molecule (needed in some form to draw comparison), so the negative charge is dispersed to a smaller extent than in the conjugate base of squaric acid, so the ethanoate ion is less stabilised, hence less acidic. (1 mark for describing ethanoic acid)

For ethanol, the negative charge on the oxygen of the conjugate base of ethanol is intensified by the inductively electron-donating alkyl group, destabilising the conjugate base, hence making ethanol the least acidic of the three. (1 mark for describing ethanol)

- Structures of the chemical compounds instead of words are accepted so long as the structures are correct.

**(f)** A notable derivative of squaric acid is dibutyl squarate. (Fig. 1.3) In order to form C-O-C (ether) bonds, an $S_N2$ reaction takes place where the **conjugate base** of an alcohol acts as a nucleophile and reacts with a suitable halogenoalkane. Hence, state the reagents needed to form dibutyl squarate from squaric acid. [2]

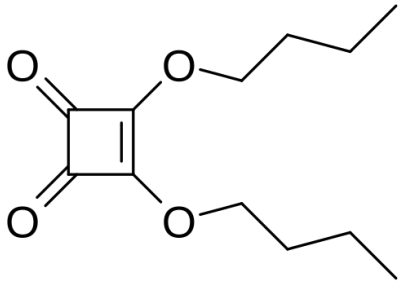



**Fig. 1.3**

Step 1: sodium metal (Na (s)), step 2: 1-bromobutane/1-chlorobutane/1-iodobutane

- If steps are not numbered, reject.
- If "chlorobutane/bromobutane/iodobutane" is given, reject. State symbols are not needed

**(g)** The divalent squarate anion is an example of the oxocarbon anion, which is a negative ion consisting solely of carbon and oxygen atoms. Each oxocarbon anion can also form a corresponding hydrogenated anion, $H_kC_xO_y^{m-}$ . Find the average oxidation number of carbon in this ion, leaving your answer in terms of k, x, y, z and m. Let z be the average oxidation number. [1]

$-m = zx+k(1) - 2(y)$ [1]

$z = \frac{2y-m-k}{x}$

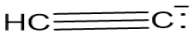
**2** Alkynes are a class of organic compounds with the general formula $C_nH_{2n-2}$. Table 2.1 shows the carbon-hydrogen bond length in ethane, ethene and ethyne.

| Molecule | Carbon–hydrogen bond length /Å |
|---|---|
| Ethane | 1.14 |
| Ethene | 1.09 |
| Ethyne | 1.06 |

**Table 2.1 (1Å = $10^{-10}$m)**

**(a)** Use the concept of hybridisation to explain the difference above. [2]
The sp hybridised carbon atom in ethyne has the highest percentage s character, followed by the $sp^2$ hybridised carbon atom in ethene and lastly, $sp^3$ hybridised carbon atom in ethane. [1] Hence, the extent of orbital overlap between the sp hybridised carbon atom and the s orbital of H atom is the largest, resulting in the shortest bond length. [1]

**(b)** Interestingly, terminal alkynes are more acidic than alkenes or alkanes, with a pKa of 25. By drawing the conjugate base of ethyne, suggest why this is so. [1]



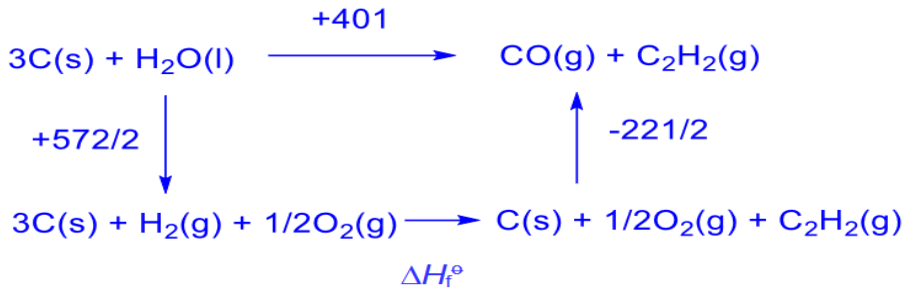
When C-H is deprotonated, the resulting carbanion is held in an orbital with 50% s-character. Since *s*-orbitals are closer to the nucleus than *p*-orbitals, this means that the electrons experience greater stabilisation from the positively charged nucleus than the conjugate bases of alkenes and alkanes. [1]

- reject if ethyne is **not** drawn with linear geometry

**(c)** Using the information in Table 2.2, calculate the standard enthalpy change of formation of $C_2H_2$. [3]

| Equation | $\Delta H^{\ominus}$/ kJ mol$^{-1}$ |
|---|---|
| $3C(s) + H_2O(l) \rightarrow CO(g) + C_2H_2(g)$ | +401 |
| $2C(s) + O_2(g) \rightarrow 2CO(g)$ | $^{-}$221 |
| $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ | +572 |

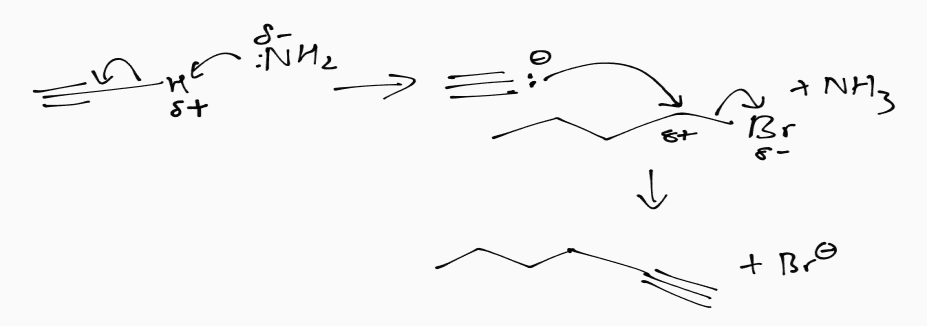
**Table 2.2**




By Hess' Law,
$\Delta H^{\ominus}_f = 401 - 572/2 + 221/2 = +225.5$ kJ mol$^{-1}$
[1] for correct energy cycle/working
[1] correct calculation WITH units and positive sign

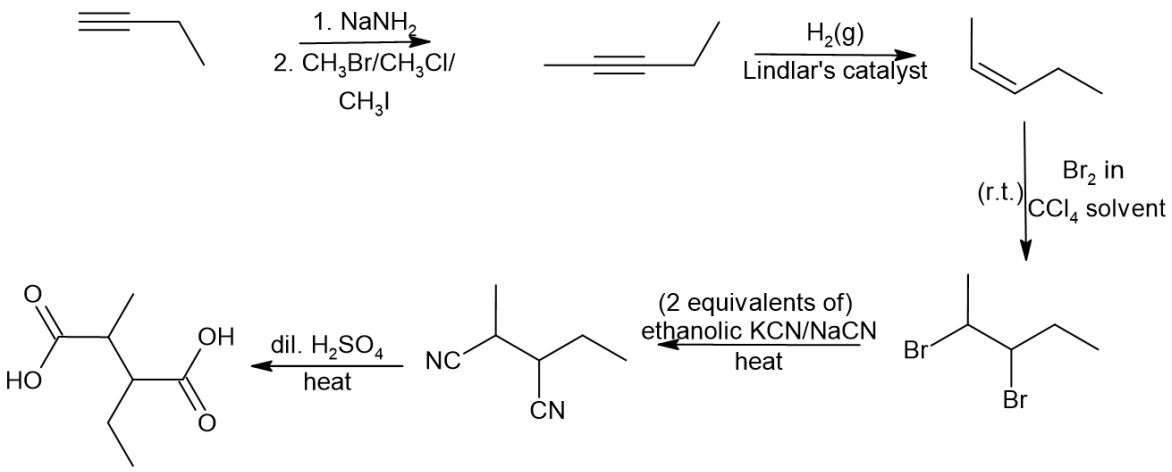
**(d)** Suggest the type of reaction alkynes tend to undergo, briefly explain. [2]
Electrophilic addition. [1] The C≡C bond is electron-rich and hence attract electrophiles, (which are electron-deficient species) [1]

**(e)** Alkynes are useful as due to their unusual acidity, it is possible to greatly increase the number of carbons on a molecule. A base known as $NaNH_2$ can be used to first deprotonate the terminal hydrogen, and the resultant species can act as a nucleophile to attack an alkyl halide in a $S_N2$, forming a new carbon-carbon bond. Using ethyne and 1−bromobutane, describe the mechanism of this reaction, showing all lone pairs, curly arrows and partial charges where necessary. [3]



- [1] correct step involving deprotonation of terminal hydrogen
- [1] correct $S_N2$ attack on electrophilic carbon
- [1] all equations are balanced ($NH_3$ and $Br^-$ in the equation)
- Deduct [0.5] for every mistake:
  - Non-linear geometry around alkyne carbon
  - Curly arrow in first step not pointing to the carbon
  - Incorrect number of carbons (obviously)
  - Missing partial charges

**(f)** Alkynes can be subsequently reduced to cis-alkenes using a poisoned lead catalyst known as Lindlar's catalyst and hydrogen. Hence, complete the synthesis route below, giving all reagents, conditions and intermediates clearly. [4]




- 2 reagents/conditions correct: 1 mark
- All reagents/conditions correct: 2 marks
- 2 structures correct: 1 mark
- All structures correct: 2 marks

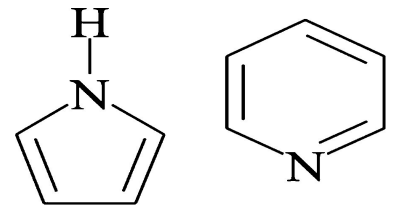
**3** Huckel's rule is such that a planar compound is aromatic if it contains (4n+2) pi electrons, where n is an integer, with a conjugated system.

**(a)** Show that benzene is an aromatic compound. [1]

Benzene has 3 pi bonds, 6 pi electrons.
$6 = 4n+2 \rightarrow n = 1$
Since n is an integer, benzene is conjugated, and planar, benzene is aromatic.

- Mathematical expression to get $n = 1$ [1]

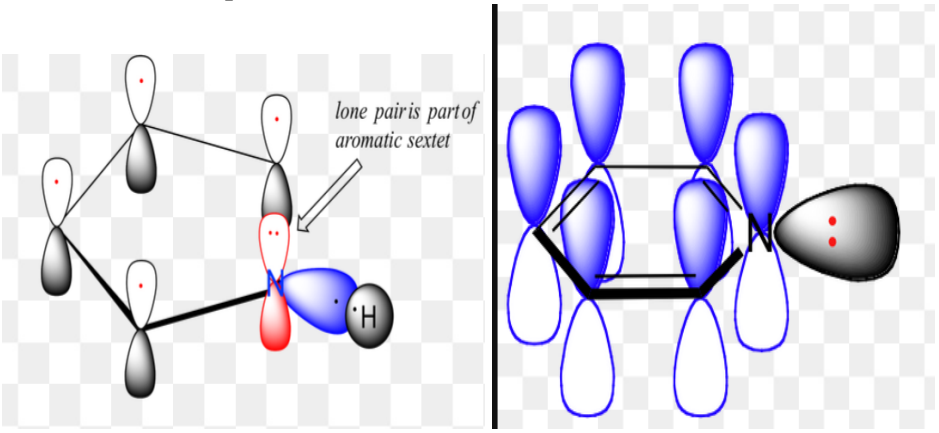
Heterocyclic compounds are extremely important in the field of organic chemistry due to them acting as building blocks in many pharmaceutical compounds. Figure 3.1 shows the structures of pyridine and pyrrole.




Pyrrole Pyridine

**Fig. 3.1**

**(b)** By drawing the atomic orbitals of the atoms in the rings of pyridine and pyrrole, predict whether both compounds are aromatic. [3]




[1] for both atomic orbitals

Pyrrole contains a $sp^3$ N atom will have one of the lone pairs reside in one of the $sp^3$ orbitals, allowing for the lone pair of electrons to participate in the aromatic system. There are 6 pi electrons, so by Huckel's rule, (where $n = 1$), pyrrole is aromatic [1]

Pyridine contains a $sp^2$ N atom will result in the lone pair of electrons residing in the unhybridised p orbital that is perpendicular to the plane of $sp^2$ orbitals, as such the lone pair of electrons on N do not overlap with the remaining aromatic system. Since there are 3 pi bonds, there are 6 pi electrons, so by Huckel's rule, (where $n = 1$), pyridine is aromatic. [1]

**(c)** Hence, deduce whether pyrrole is a strong or weak base. [2]

Weak base. [1] Since the lone pair of electrons on N are delocalised, the lone pair of electrons are less available for accepting a proton, and so it is a weak base. [1]

**(d)** Given your answer in **(c)**, deduce whether the conjugate acid of pyridine is stronger or weaker than the conjugate acid of pyrrole. [2]

The conjugate acid of pyridine is **weaker** than the conjugate acid of pyrrole. [1] The conjugate acid of pyrrole results in the loss of aromaticity, [1] and so is extremely unstable, and as such will protonate readily to re-form pyrrole.

- Reject any answer that says "because weak base, therefore strong conjugate acid" as it is not chemically ambiguous and not a rigorous explanation of **the factors** that determine strength of acid/base, namely stability.

**(e)** Pyridine does not undergo electrophilic aromatic substitution reactions **as** readily as benzene. Suggest a reason for this phenomenon. [1]

Nitrogen is electronegative/electron-withdrawing, and so decreases electron density in the aromatic ring. As a result, the benzene ring attracts electrophiles less strongly compared to benzene. [1]

The Chichibabin reaction is an example of nucleophilic aromatic substitution, where the nucleophile attacks the aromatic ring. Figure 3.2 shows an example of such a reaction.

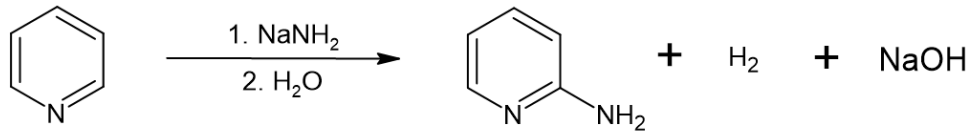
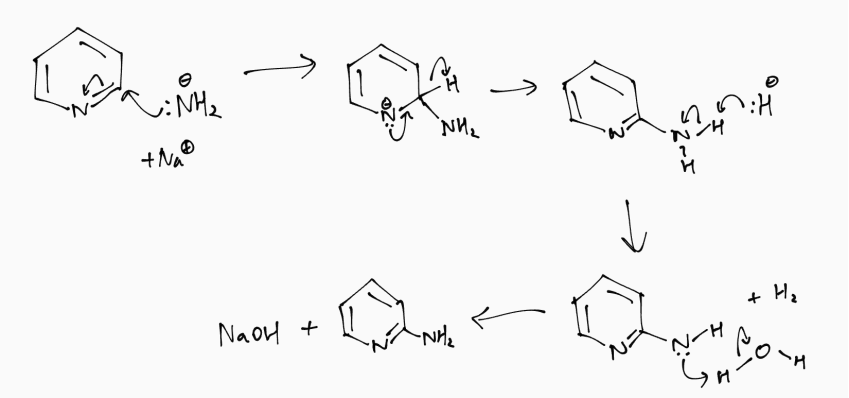



**Fig. 3.2**

**(f)** Describe the mechanism of this reaction, showing all curly arrows and lone pairs where possible. This reaction involves the removal of a $H^-$ as part of its steps. Additionally, the final product is also an intermediate in the reaction, i.e. it is formed twice. [3]




[1] All curly arrows are correct and pointing to the correct atom (not to the charge)
[1] All equations are balanced
[1] All lone pairs accounted for

**(g)** Pyrroles are components of more complex macrocycles, one of which is heme, a major component of hemoglobin, itself a major component of blood. Suggest why blood in living organisms must be a buffer. [1]

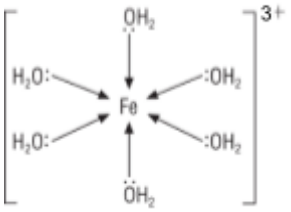
Enzymes in living organisms are pH-sensitive and have an optimal pH, hence for the living organism to continue functioning, blood must be a buffer.

This is a "suggest" question, so long as the answer is chemically sound, it is accepted.

**4** Pure metals are important in the world, be it the past or the present. In the past, pure metals were used to create dyes, such as green (copper arsenite), blue (calcium copper tetrasilicate) et cetera.

**(a)** M is a transition metal. When $M^{n+}$ is in the gaseous state, it is colourless. However, when dissolved in water, it produces a yellow colour solution. Suggest the name of M, the value of n, and by drawing the displayed structure of the complex in water, explain this phenomenon **in detail**. [4]

M is iron, and n = 3. [1] (rej. if "Fe"/ "$Fe^{3+}$" given). In the presence of water ligands, the partially filled degenerate 3d orbitals of the $Fe^{3+}$ ion are split into two different energy levels [1] with a small energy gap between them. There are vacancies in the higher energy d orbitals. The promotion of an electron from the lower to the higher of these d orbitals requires the absorption of radiation in the visible spectrum/light with energy corresponding to the energy gap. Such a d-d transition is responsible for the yellow colour of the complex ion. The yellow observed is the complement of the colours absorbed. [1] (accept: absorption of purple/violet light)




[1] for correct structure

The thermite reaction was, and still is, one of the most used ways to abstract pure metals. A thermite reaction is an exothermic redox reaction between Al and a metal oxide. An example is shown below:

$$Fe_2O_3 + 2\,Al \longrightarrow 2\,Fe + Al_2O_3$$

**Equation 4.1**

**(b)** Suggest, in terms of bond formation, why this reaction reaches extremely high temperatures. [1]

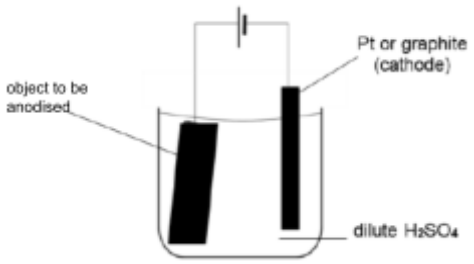
Aluminum forms stronger and more stable bonds with oxygen than iron. [1]

- Any reasonable explanation related to bond formation will be accepted.

**(c)** Considering Equation 4.1, if an initial reaction mixture consists of 40.0g of $Fe_2O_3$ and 40.0g of Al, calculate the mass of Fe produced upon the completion of the reaction. [2]
$^{n}Al = 40.0/27.0 = 1.48148 mol$, $^{n}Fe_2O_3 = 40.0/159.6 = 0.250627$ mol, $Fe_2O_3$ is the limiting reagent. [1] for both calculations.

$^{n}Fe$ produced = 2*0.250627=0.501254 mol
Mass of Fe produced = 0.501254*55.8=27.97 g = 28.0g (3sf) [1]
- Deduct 1 mark if answer is not left to 2 or 3 sf

**(d)** $Al_2O_3$, or slag, is an important component in electronics. Draw a labelled diagram describing the anodisation of aluminium and briefly outline **one** benefit of this process. Label the anodised object, "object to be anodised".[3]




[1] Cathode is correct
[1] Anode is correct
[1] Electrolyte and battery present and correct

**(e)** State the chemical equation, with state symbols, of the reaction between slag and excess aqueous KOH. [2]

$Al_2O_3\ (s) + 2OH^-\ (aq) + 3\ H_2O\ (l) \rightarrow 2\ [Al(OH)_4]^-\ (aq)$

Deduct 1 mark if state symbols not given for any compound

**5** Piranha solution is a mixture of concentrated $H_2SO_4$ and $H_2O_2$. It is a **strong** oxidant and a **strong** acid that can dissolve organic compounds. It is used in laboratories only as a last resort for stubborn organic residue. It first begins with the generation of an acid known as Caro's acid as shown:

**Fig. 5.1**

Afterwards, a series of radical reactions occur as shown:

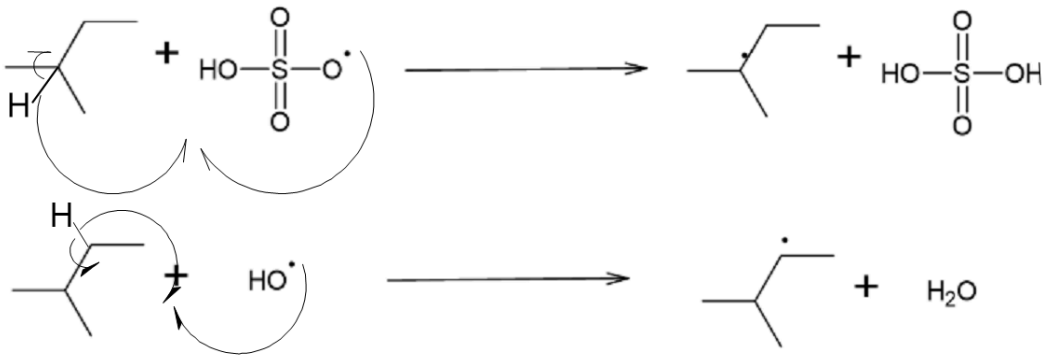
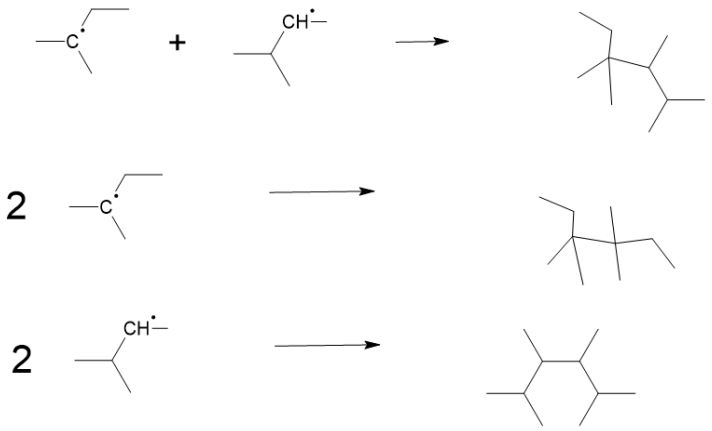


**Fig. 5.2**

**(a)** Draw a series of curly arrows on Figure 5.2 to demonstrate how the reaction occurs. These are two distinct steps. [2]

- Use of half-arrows correctly (award 1 mark per reaction)

**(b)** State an equation that terminates the reaction above with a hydrocarbon product. You are allowed to use skeletal structures. [1]



- Any of the three is accepted provided 1. # of carbons is correct. 2. arrangement of bonds is correct
- As the question stem contained "hydrocarbon product", products with any other atoms but carbon and hydrogen are rejected.

Caro's acid is a very strong oxidant, demonstrated by its standard electrode potential of $E^{\ominus}$ = +2.51 V. Caro's acid has been industrially used to oxidise cyanide ions found as waste products in gold mining. The following equation is for this reaction:

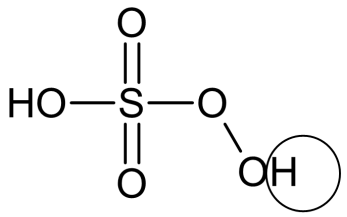
$$H_2SO_5 + CN^- \rightarrow OCN^- + SO_4^{2-} + 2H^+$$

**(c)** Given that the $E^{\ominus}$ of $CN^-$ is $-0.57$V, determine whether this reaction is spontaneous. [1]

$H_2SO_5$ will be reduced, $CN^-$ gets oxidised.
$E_{cell}$ = +2.51 -(-0.57) = +3.08V [½]

Since $\Delta G^{\ominus} = -nFE^{\ominus}$ where n and F are positive numbers, $\Delta G^{\ominus}$ is negative
-> This reaction is spontaneous. [½]

**(d) (i)** $H_2SO_5$ is a dibasic acid. The pKa values of the 2 hydrogens are 1 and 9.3 respectively. Copy the structure of $H_2SO_5$ from Fig. 5.1 and circle the hydrogen with a pKa of 9.3. [1]



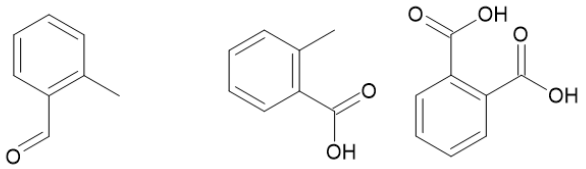

[1] Given to correct hydrogen **circled** (if a circle wasn't used (for some reason), deduct 1 mark)

**(e)** An alkali metal salt of $H_2SO_5$, known as oxone, is a common **oxidant** used in organic chemistry. Compound **A** with molecular formula $C_8H_8O$, produces a silver mirror when warmed with a solution of diamminesilver (I) complex, $[Ag(NH_3)_2]^+$. However, it does not produce a brick red precipitate when warmed with Fehling's reagent. When oxone is reacted with compound **A**, it produces a compound **B** that will effervesce upon reacting with sodium metal, producing 0.5mol of $H_2$ gas per mole of **B**. When compound **A** is reacted with hot, acidified $KMnO_4$, it produces a symmetrical molecule, compound **C**. Suggest structures for **A** – **C** and explain the reactions described above. [4]

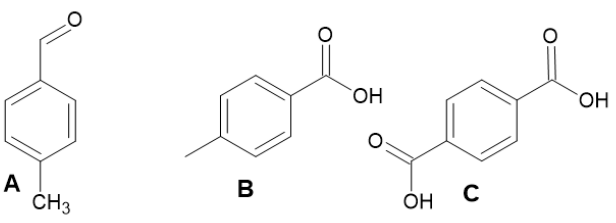
| Observation | Explanation |
|---|---|
| A has a low C:H ratio | A contains a benzene ring |
| A produces a silver mirror upon warming with Tollens' reagent | A is oxidised [0.5] by Tollens' reagent. A contains an aldehyde group [0.5] |
| A does not produce a brick red ppt. with Fehling's reagent | A is not oxidised. (not credited, but if this missing, deduct 0.5m) A is a benzaldehyde derivative [0.5] (accept if the structure of benzaldehyde is drawn) |
| A produces B when oxone is added | A is oxidised to B, B contains **one** carboxylic acid group. [0.5] |
| B will effervesce with sodium metal to produce 0.5mol of $H_2$ per mole of B. | Redox [0.5] reaction occurs between B and sodium metal. Confirms B has **one** carboxylic acid group* (the 0.5m for carboxylic acid in the first part can be given here instead) |
| A produces a symmetrical molecule when reacted with hot, acidified $KMnO_4$ | A is oxidised. A is di-substituted at the 1,2 **or/and** 1,4 positions [0.5] (If candidate writes either one, or writes both, credit) |

- Maximum of 2 marks given for observations.

Structures: 1 mark if 2 structures correct, 2 marks if all 3 structures correct




**All** top must be correct **OR all** bottom must be correct



**(f)** The standard cell potential of the $HSO_5^-/HSO_4^-$ couple is +1.8V against the standard hydrogen electrode.

**(i)** Define the standard cell potential. [2]

It is the potential difference between two half cells [1]measured at standard conditions, i.e. 298K, 1 bar for gases and 1 mol $dm^{-3}$ for solutions [1]

- Usually a question like this only takes up about a mark, the mark should act as a guide to the amount of detail to include!

The Nernst equation is the mathematical expression used to find the standard cell potential at non-standard conditions. It is given as:

$$E = E^{\ominus} - \left(\frac{RT}{nF}\right) \ln Q$$

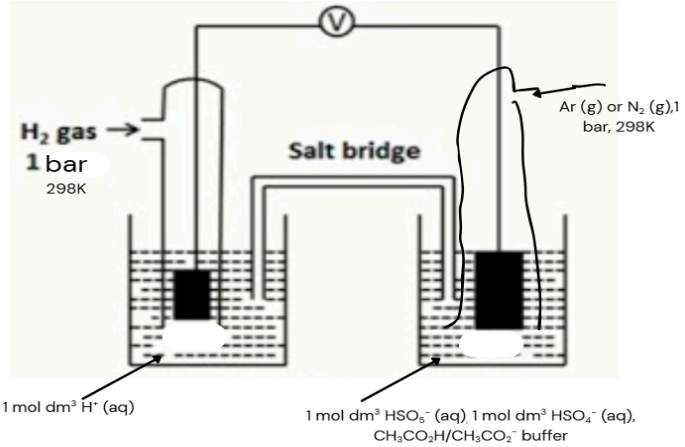
where Q is the equilibrium constant ($K_c$), T is the temperature in kelvin, n is the amount of electrons and F is Faraday's constant. The half-equation for the $HSO_5^-/HSO_4^-$ couple is given to be $HSO_5^-$ (aq) + $2H^+$ (aq) + $2e^-$ ⇌ $HSO_4^-$ (aq) + $H_2O$ (l)

**(ii)** State an expression for the non−standard cell potential of this half-cell in terms of $[HSO_5^-]$ and $[HSO_4^-]$ at 25°C. You are not required to state the units. [1]

$E = (+)1.8 - 0.0128ln\frac{[HSO_4^-]}{[HSO_5^-]}$ [1]

Oxone must be used as an aqueous solution of $HSO_5^-$ because a solution of $HSO_5^-$ (aq) is too unstable. The $HSO_5^-/HSO_4^-$ electrolyte **must** also be prepared in an $CH_3CO_2H/CH_3CO_2^-$ pH buffer and continuously purged with any **inert** gas in order to create an oxygen-free half-cell.

**(g)** Sketch a labelled diagram of how an experiment can be done to determine the standard cell potential of the $HSO_5^-/HSO_4^-$ half cell. [4]




- [1] for voltmeter and salt bridge
- [1] Correct standard hydrogen electrode drawing **and** labelling
- [1] Correct choice of inert gas
- [1] Correct half cell drawn **and** correct labelling

**6** An important Lewis acid catalyst in the field of organic chemistry is anhydrous $AlCl_3$.

**(a)** By drawing structures of $AlCl_3$ and $[AlCl_4]^-$, suggest why $AlCl_3$ is a Lewis acid. [2]

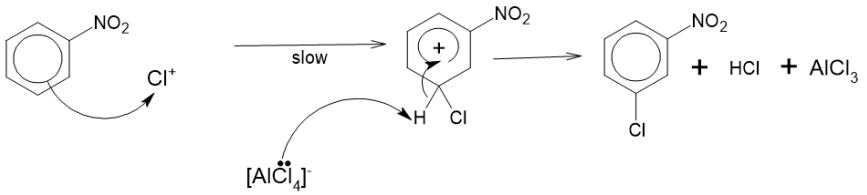

[1] Correct structure drawn **with** correct geometry, coordinate bond, and negative charge

$AlCl_3$ is electron-deficient and so can accept a pair of electrons [1] to complete the octet about the Al atom.

(b) Describe a mechanism of the reaction between nitrobenzene and chlorine gas, showing all curly arrows, lone pairs and partial charges. [4]

Electrophilic Substitution

$AlCl_3 + Cl_2 \rightarrow [AlCl_4]^- + Cl^+$




- [1] Name of mechanism spelled correctly
- [1] Correct movement of electrons
- [1] Correct intermediate (must be 1,3 substituted since $-NO_2$ is 3-directing group)
- [1] Correct slow/fast step + regeneration of catalyst
  Arrows always start from an electron source and end somewhere electron-deficient (electron sink), so arrows cannot point to charges, or the middle of nowhere

**(c)** By writing **one** suitable equation, suggest why the reaction above will not take place if the system were not anhydrous. [2]

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)^6]^{3+} + 3Cl^{-}$ [1]

Since the Al atom will be surrounded by (six) coordinatively bonded water ligands, the Al atom will not be able to accept an electron pair and work as a Lewis acid to form the $Cl^{\pm}$ electrophile. [1]

- The hydrolysis equation is not needed since it does not answer the question and writing it will deduct 0.5m as the question only asked for one equation.
- The question must be answered in context of the reaction above. If generic answers are given, no mark awarded.
- State symbols not needed, but it is okay to write them **so long** as they are correct
  - $AlCl_3$ (s), $H_2O$ (l), $[Al(H_2O)^6]^{3+}$ and $Cl^{-}$ (aq)
  - If incorrect for any species, deduct 0.5m