IDK Junior College

CANDIDATE NAME

CHEMISTRY
9476/02 **2 hours**

Additional Material(s): Data Booklet

READ THE FOLLOWING FIRST
Write in dark blue or black ink.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Answer **all** questions in the spaces provided.

You are reminded that there is extra working space on pages 15 & 16. Do write the question number and part clearly.

The use of a scientific calculator is expected, where appropriate.
You are reminded of the need for good English and legible handwriting.

The number of marks is given in brackets [ ] at the end of each question or part question.

For examiner's use	
1	/11
2	/15
3	/13
4	/12
5	/16
6	/8
Deductions	**sf:** **structures:** **units:**
Total	/75

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.

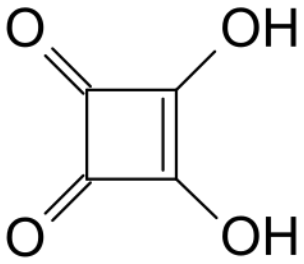


Fig. 1.1

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

.....

(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]

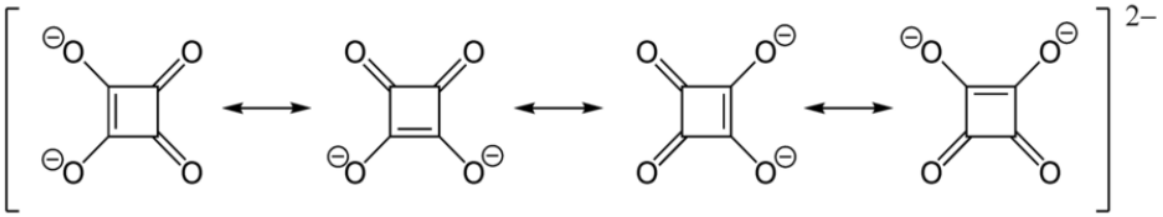


Fig. 1.2

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

.....

.....

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

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

.....

.....

.....

.....

.....

.....

.....

.....

(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]

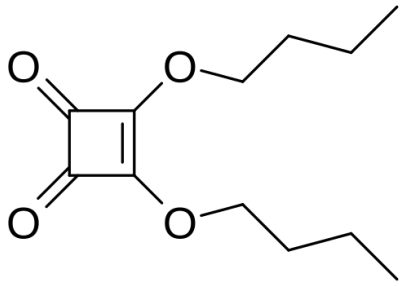


Fig. 1.3

.....

(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]

[Total: 11]

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]

.....

.....

.....

(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]

.....

.....

(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

(d) Suggest the type of reaction alkynes tend to undergo, briefly explain. [2]

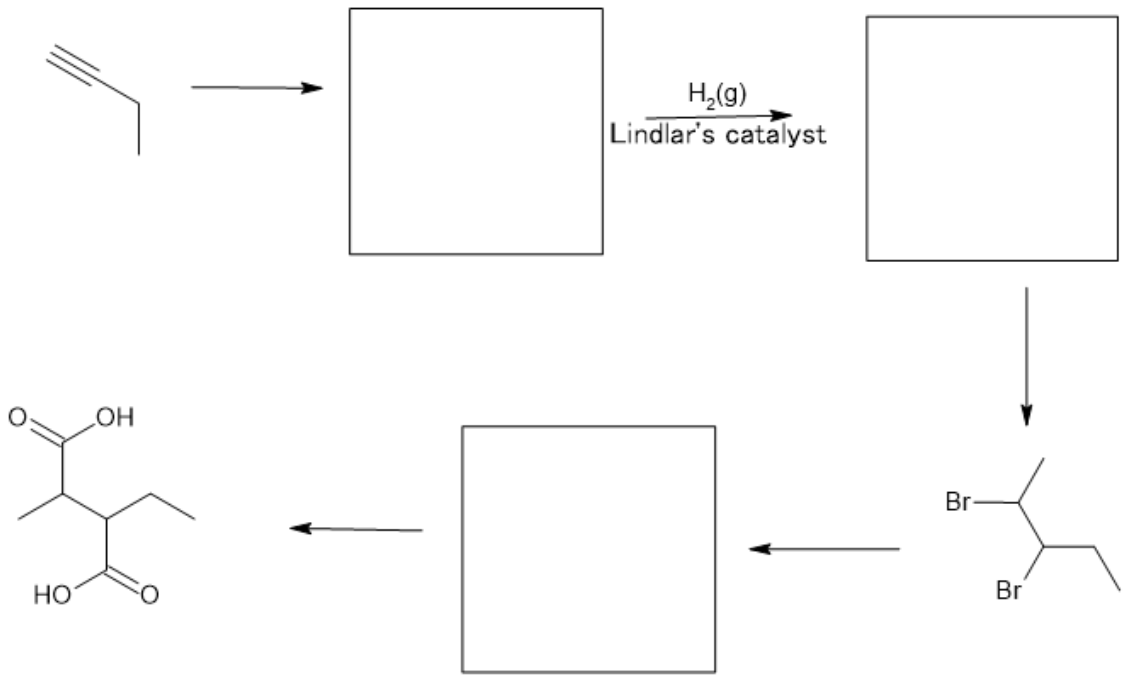
.....

.....

.....

(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]

(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]

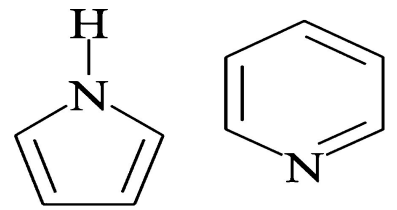


[Total: 15]

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]

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, given that both compounds are planar.[3]

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

.....

.....

.....

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

.....

.....

.....

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

.....

.....

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

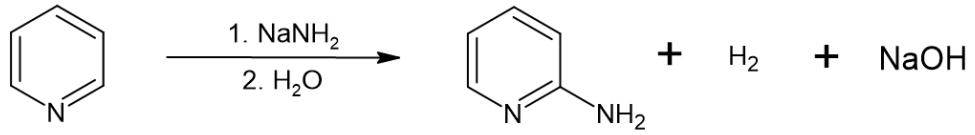


Fig. 3.2

(f) Describe the mechanism of this reaction, showing all curly arrows, partial charges 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]

(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]

.....

.....

[Total: 13]

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]

.....

.....

.....

.....

.....

.....

.....

.....

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:

$$\mathrm{Fe_2O_3 + 2\,Al \longrightarrow 2\,Fe + Al_2O_3}$$

Equation 4.1

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

.....

.....

(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]

(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. [3]

.....

.....

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

.....

[Total: 12]

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:

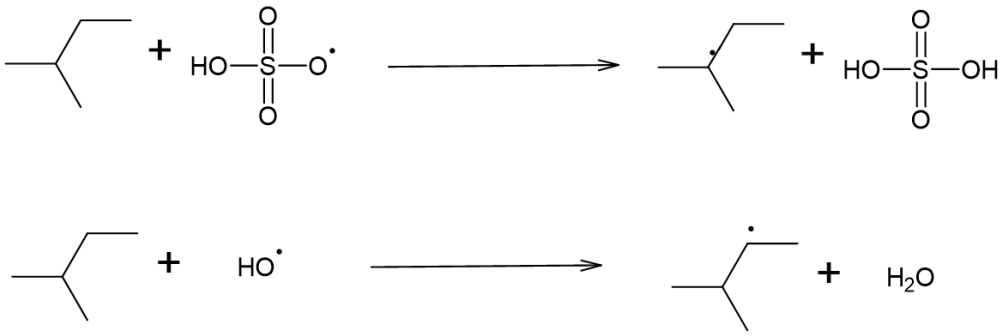


Fig. 5.2

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

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

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 -0.57V, determine whether this reaction is spontaneous. [1]

(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]

(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]

(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]

……

……

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]

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]

[Total: 16]

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]

.....

.....

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

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

.....

.....

[Total: 8]

Extra Writing Space

You are reminded to indicate your question number and part clearly.

The End