

Examiners' Report
January 2012

GCE Chemistry 6CH05 01

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Introduction

The paper was accessible though some questions seemed to challenge many candidates.

Question 21 (a)

Electronic configuration of transition metals was usually well known. Some did not realise the stability of half filled shells, while some thought both elements had five 3d electrons.

21 (a) Chromium is a typical transition metal, although its electronic configuration does **not** fit the general trend found in the first transition series.

Complete the electronic configurations in *s,p,d* notation for vanadium and chromium.

(1)

Vanadium: [Ar] $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

Chromium: [Ar] $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$



ResultsPlus

Examiner Comments

Here the candidate has given the full configurations correctly. This was not penalised but gave them unnecessary work.



ResultsPlus

Examiner Tip

Read the question to avoid unnecessary work.

21 (a) Chromium is a typical transition metal, although its electronic configuration does **not** fit the general trend found in the first transition series.

Complete the electronic configurations in *s,p,d* notation for vanadium and chromium.

(1)

Vanadium: [Ar] $3d^5$

Chromium: [Ar] $4s^2 3d^4$



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Examiner Comments

This is an odd answer, giving a half filled 3d shell for vanadium, but not for chromium.



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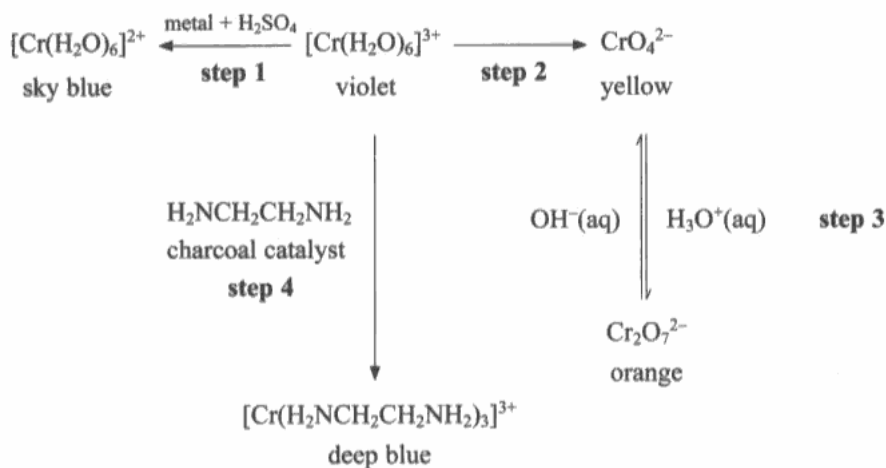
Examiner Tip

Learn the configuration rules thoroughly, the only variations to the normal shell filling principle are where the atom would be one electron short of a half filled or filled shell.

Question 21 (b) (i)

The key phrase in this question, missed by many candidates is 'in the diagram above'. As a result catalytic activity and other physical properties were not rewarded.

(b) Some interconversions found in the chemistry of chromium are shown below. Use this information to answer the questions that follow.



(i) State **two** typical properties of transition metals, other than the formation of coloured ions, which are shown in the diagram above.

(2)

- They have multiple oxidation states.
- Incompletely-filled d-orbital so ligand exchange takes place.



ResultsPlus
Examiner Comments

The first point is fine.

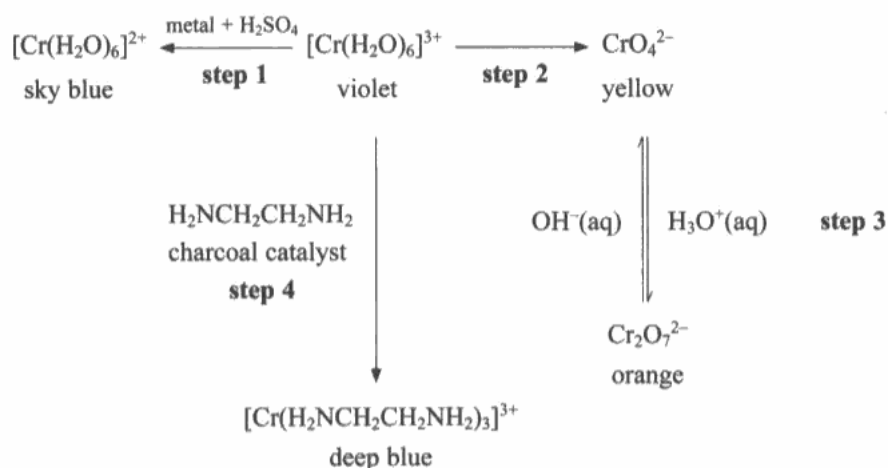
The second needs to be expressed as 'complex formation' to gain credit.



ResultsPlus
Examiner Tip

Read the question and give the obvious answers.

(b) Some interconversions found in the chemistry of chromium are shown below. Use this information to answer the questions that follow.



(i) State **two** typical properties of transition metals, other than the formation of coloured ions, which are shown in the diagram above.

Catalytic activity. Multiple oxidation numbers. Paramagnetic⁽²⁾



ResultsPlus Examiner Comments

This is high risk. Three answers are given and **all** must be correct to gain 2 marks. Fortunately catalytic activity was regarded as neutral. They are not all paramagnetic.



ResultsPlus Examiner Tip

Do not use the scatter gun approach giving several answers in the hope that one or two may be correct.

Question 21 (b) (ii)

The popular choice here was zinc, with a cell value of 0.35 V.

Alkali metals were penalised as they would also react vigorously with water, so only one mark was then available.

There were calculation errors, significant figures lost, and sometimes just a failure to identify the metal despite a correct calculation.

(ii) Use E^\ominus values from your data booklet to suggest a metal that could be used for step 1. Justify your answer by calculating E^\ominus for your cell. (2)

Mn^{2+} could be used. -0.41

$$E^\ominus_{\text{cell}} = \text{Reduction} - \text{oxidation}$$
$$= -0.41 - (-0.19)$$
$$~~+0.78~~ = +0.78 \text{ V}$$


ResultsPlus
Examiner Comments

Notice how the ion has been given rather than the metal, which would not work. However, the correct calculation gets one mark.



ResultsPlus
Examiner Tip

The question asks for the metal.

(ii) Use E^\ominus values from your data booklet to suggest a metal that could be used for step 1. Justify your answer by calculating E^\ominus for your cell.

E^\ominus for the cell is -0.41 V . Zn could be used as the metal as its E^\ominus is -0.76 V due to the rule of electrons flowing from the more negative to the positive (2)



ResultsPlus
Examiner Comments

Zinc has been chosen correctly, but the calculation of E for the cell has not been done.



ResultsPlus
Examiner Tip

Check each question has been fully answered before going on to the next.

Question 21 (b) (iii)

The most common error was to say the oxidation number of chromium does not change, without giving the value, +6.

Some answers used incorrect language referring to total oxidation number as -2, which is the algebraic sum of the oxidation numbers or the charge on the ion.

Some thought oxygen changed its oxidation number.

(iii) Explain, using oxidation numbers, whether or not the conversion in **step 3** is a redox reaction.

(2)

No. The oxidation number of chromium in CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ does not change during the reactions, so the reactions are not redox ones.



ResultsPlus
Examiner Comments

The conversion has been recognised as not redox because oxidation number has not changed, but actual oxidation numbers have not been calculated.



ResultsPlus
Examiner Tip

Give as much relevant information as you can.

Question 21 (b) (iv-v)

Only weak candidates did not realise that bidentate ligands form two bonds per ligand in part (iv).

Many thought hydrazine contained a double bond and/or had only one or no lone pairs of electrons in part (v).

- (iv) The organic compound $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ that is used in **step 4** is 1,2-diaminoethane, often called ethylenediamine. It is a **bidentate ligand**. Explain the meaning of this term.

(1)

A ligand which donates two lone pair of electrons to the central metal to form a dative covalent bond is called a bidentate ligand.

- (v) Explain, in terms of its structure, how $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ can act as a bidentate ligand whereas H_2NNH_2 cannot.

(2)

$\text{H}_2\ddot{\text{N}}\text{CH}_2\text{CH}_2\ddot{\text{N}}\text{H}_2$ has two lone pair of electrons on the nitrogen atom when H_2NNH_2 does not have lone pair of electrons of N because of the double bond.



ResultsPlus Examiner Comments

This is quite a common response. Part (iv) is fine, but in part (v) the candidate does not realise that hydrazine has two lone pairs of electrons. In this case they have decided it contains two four valent nitrogens with a double bond.



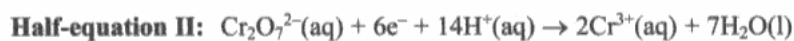
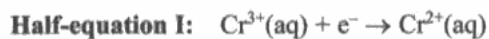
ResultsPlus Examiner Tip

Remember nitrogen usually forms three bonds.

Question 21 (c) (i)

Very few candidates did not look up and record the values with signs correctly.

(c) The half-equations relating the interconversion of the species $\text{Cr}^{2+}(\text{aq})$, $\text{Cr}^{3+}(\text{aq})$ and $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ are given below.



(i) Use your data booklet to find E^\ominus for each of the above half-equations.

(1)

Half-equation I - 0.41 Volts

Half-equation II - 0.13 Volts



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Examiner Comments

The wrong value and sign are given here, the value for chromate(VI), not dichromate(VI) has been given.

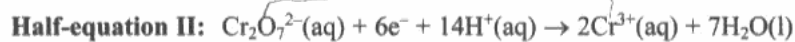
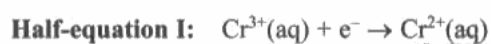


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Examiner Tip

Check the precise half equation is correct when looking up electrode potentials.

(c) The half-equations relating the interconversion of the species $\text{Cr}^{2+}(\text{aq})$, $\text{Cr}^{3+}(\text{aq})$ and $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ are given below.



(i) Use your data booklet to find E^\ominus for each of the above half-equations.

(1)

Half-equation I *- 0.41* Volts

Half-equation II *1.33* Volts



ResultsPlus
Examiner Comments

The positive sign is missing



ResultsPlus
Examiner Tip

Entropies, enthalpies, and electrode potentials must have signs even if positive.

Question 21 (c) (ii)

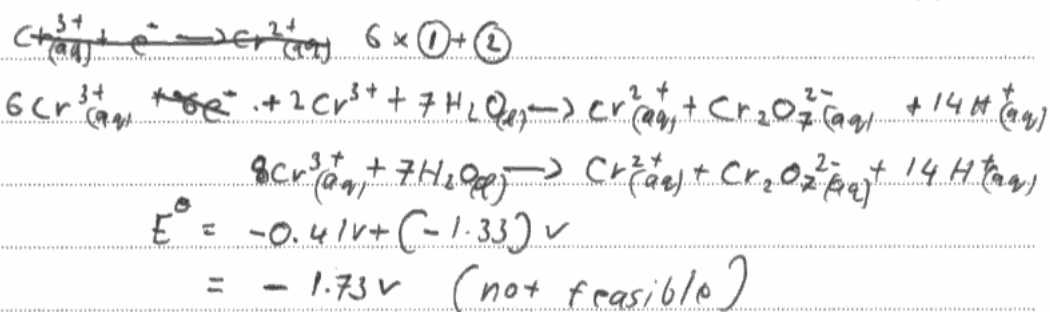
The equation proved testing as it is not the direction followed by the spontaneous reaction. Even when the correct sequence was given balancing was also challenging.

Handling the redox potentials to get E cell also proved difficult, though the interpretation of the result was straightforward providing the question was read correctly and information about the disproportionation reaction was given.

*(ii) Write the overall equation for the disproportionation of Cr^{3+} into Cr^{2+} and $\text{Cr}_2\text{O}_7^{2-}$.

Use the E^\ominus values you have obtained in (c)(i) to show whether or not this disproportionation is feasible under standard conditions.

(4)



ResultsPlus Examiner Comments

Here the candidate has managed the correct equation with one slip and forgotten that 6 Cr^{2+} ions form. They have then made an arithmetic error, but managed the correct interpretation.



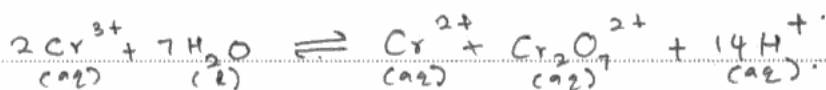
ResultsPlus Examiner Tip

Practise balancing equations for redox reaction using oxidation numbers. Check arithmetic after each step.

*(ii) Write the overall equation for the disproportionation of Cr^{3+} into Cr^{2+} and $\text{Cr}_2\text{O}_7^{2-}$.

Use the E^\ominus values you have obtained in (c)(i) to show whether or not this disproportionation is feasible under standard conditions.

(4)



$$E^\ominus = E_{\text{red}}^\ominus - E_{\text{oxi}}^\ominus$$

$$= (+1.33) - (-0.41)$$

$$= +1.74$$

It is feasible.



ResultsPlus Examiner Comments

The entities in the equation are correct but there is no attempt to balance it. There is an error in the calculation, but the result is correctly interpreted.



ResultsPlus Examiner Tip

Practise balancing equations for redox reaction using oxidation numbers and practice E cell calculations for reactions that are not spontaneous.

Question 22 (a) (i)

This was usually answered successfully. The best method is to divide percentages by the appropriate relative atomic mass. Credit was given for calculating the molar mass and then calculating moles from the percentages.

22 (a) Tiglic acid is a compound that is used as a defensive agent by some beetles.

- (i) Tiglic acid contains, by mass, 60% carbon, 8% hydrogen, with the remainder being oxygen. Show that these data are consistent with the formula $C_5H_8O_2$.

(1)

	C	H	O
mass :	60%	8%	32%
moles :	5	8	$\frac{32}{16} = 2$
mole ratio :	5	8	2

Empirical formula is $C_5H_8O_2$ which is consistent with the formula given.



ResultsPlus Examiner Comments

This candidate has been penalised for failing to show what they are doing to the carbon and hydrogen percentages.



ResultsPlus Examiner Tip

Always show your working clearly.

22 (a) Tiglic acid is a compound that is used as a defensive agent by some beetles.

- (i) Tiglic acid contains, by mass, 60% carbon, 8% hydrogen, with the remainder being oxygen. Show that these data are consistent with the formula $C_5H_8O_2$.

(1)

$$C = 12 \text{ amu}$$

$$H = 1 \text{ amu}$$

$$O = 16 \text{ amu}$$

$$5 \times 12 = 60$$

$$8 \times 1 = 8$$

$$2 \times 16 = 32$$

$$60 + 8 + 32 = 100 \text{ amu}$$

$$60\% \text{ of } 100 = 60 \text{ amu}$$

$$8\% \text{ of } 100 = 8 \text{ amu}$$

Oxygen is remainder
(32 amu)



ResultsPlus
Examiner Comments

This is the correct second method.



ResultsPlus
Examiner Tip

The method dividing percentages by molar masses is best.

Question 22 (a) (ii)

The test for a carbon-carbon double bond is well known but must be precisely stated, bromine water changes from yellow/brown to colourless.

The most common test given for a carboxylic acid was phosphorus(V) chloride. This is not conclusive as an alcohol gives the same result, so no credit was given. The best test is that a large volume of sodium carbonate solution can be neutralized.

(ii) Tiglic acid contains a carbon-carbon double bond and a carboxylic acid group.

Suggest **one** test for each of these groups in tiglic acid. State what you would do and what you would see as a positive result for the tests. (4)

Test for C=C Add Bromine water.
- Brown solution decolourises.

Test for —COOH Add ~~2,4 dinitro~~ Add methanol CH₃OH.
- Fruity smell forms from ester, formed.



ResultsPlus Examiner Comments

The test for a carbon-carbon double bond is fine. Ester formation requires concentrated sulfuric acid and heat so a mark was lost here.



ResultsPlus Examiner Tip

Always give reaction reagents and conditions in full in this type of question.

(ii) Tiglic acid contains a carbon-carbon double bond and a carboxylic acid group.

Suggest **one** test for each of these groups in tiglic acid. State what you would do and what you would see as a positive result for the tests.

(4)

Test for C=C mix with a small quantity of bromine,
the orange/brown solution will decolourise as a
positive result.

Test for -COOH mix with sodium hydroxide, a white
precipitate indicates a positive result.



ResultsPlus

Examiner Comments

The test for a carbon-carbon double bond is incomplete. Bromine rather than bromine water is used but the colour change is given. Though sodium hydroxide does neutralize a carboxylic acid, it is not a unique test, so no credit is given.



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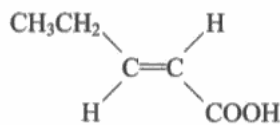
Examiner Tip

Learn details of tests for all major functional groups.

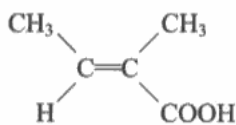
Question 22 (b) (i)

The understanding and application of E/Z nomenclature proved challenging. Good candidates got the reasoning mark by discussing priority in terms of atomic numbers.

(b) It is suggested that the structure of tiglic acid is either that of **A** or **B**.



A



B

(i) State, with a reason, whether **B** is the *E*- or *Z*- isomer.

(2)
B is an *E*- isomer because the molecules of most importance are not on the same side of the double bond.

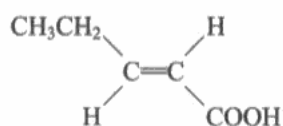


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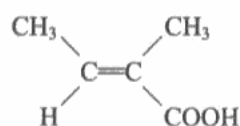
Examiner Comments

This is an example of poor language costing a mark. The correct term is attached group or functional group, not molecule.

(b) It is suggested that the structure of tiglic acid is either that of **A** or **B**.



A



B

(i) State, with a reason, whether **B** is the *E*- or *Z*- isomer.

(2)

Z isomer as the identical group, CH₃ is at the same side.



ResultsPlus
Examiner Comments

The most common wrong answer, totally confusing *E/Z* with cis/trans.

Question 22 (b) (ii-iii)

Common errors were the omission of charges or wrong numbers of hydrogens in the fragment formulae.

(ii) Tiglic acid contains a carbon-carbon double bond and a carboxylic acid group.

Suggest **one** test for each of these groups in tiglic acid. State what you would do and what you would see as a positive result for the tests.

(4)

Test for C=C Add Bromine water.

- Brown solution decolourises.

Test for —COOH Add ~~2,4~~ dinitro Add methanol CH₃OH.

- Fruity smell forms from ester_y formed.



ResultsPlus

Examiner Comments

The carbon chain fragment is two hydrogens short.



ResultsPlus

Examiner Tip

Check that carbons have sufficient bonds in each formula.

(ii) The mass spectrum of tiglic acid shows two prominent peaks at mass/charge ratios 45 and 55. Write the formulae of the fragments giving rise to each of these peaks.

(2)

45 COOH

55 $\text{CH}_3\text{CH}_2\text{CCH}_3$

(iii) Does this data from the mass spectrum **alone** enable you to decide which of **A** or **B** is the structure of tiglic acid? Explain your answer.

(1)

No, we need to see the other peaks. If there are any additional peaks for example,

Also, if we know the M peak we could see if the Mr is the same.



ResultsPlus
Examiner Comments

No charges on the ions and no mention of the same peaks.



ResultsPlus
Examiner Tip

In mass spectrometers fragments are always positive ions.

Question 22 (c) (i-ii)

There was often a lack of clear reasoning from the tests in (i).

The application of *E/Z* in (ii) was beyond most candidates.

- (c) The position of a C=C double bond in a molecule can be determined by ozonolysis. The compound is reacted with ozone and then dilute acid, two carbonyl compounds being produced as shown below.

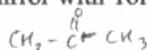


Ozonolysis of tiglic acid gives two carbonyl compounds, C and D.

Compound C gives a silver mirror with Tollens' reagent and gives iodoform with iodine in alkali.



Compound D does **not** give a silver mirror with Tollens' reagent, but does give iodoform with iodine in alkali.



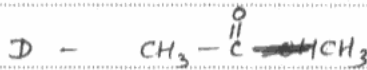
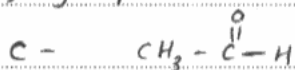
- * (i) From the results of the experiments, deduce the functional groups present in C and D. By considering the two possible structures for tiglic acid, give the structural formulae of C and D.

From the structures you have drawn, state which of the structures A or B could represent tiglic acid.

(6)

Compound C should contain an aldehyde group to give positive results for the reaction with Tollens' reagent.

And there has to be a $-\text{CH}_3$ group attached to the carbon at carbonyl carbon atom. Since compound D gives negative results for the reaction with Tollens' reagent it should contain a ketone with a carbonyl carbon which a $-\text{CH}_3$ group is attached. Therefore D should be a ketone.



Structure A should be tiglic acid.

- (ii) Explain whether or not these tests show definitely that your answer to (c)(i) represents tiglic acid.

(1)

Yes. Because the structure B cannot produce these 2 compounds. (C and D)



ResultsPlus Examiner Comments

Here the excellent reasoning compensates for two errors in formulae.



ResultsPlus Examiner Tip

Always show your reasoning as fully as possible.

- (c) The position of a C=C double bond in a molecule can be determined by ozonolysis. The compound is reacted with ozone and then dilute acid, two carbonyl compounds being produced as shown below.



Ozonolysis of tiglic acid gives two carbonyl compounds, C and D.

Compound C gives a silver mirror with Tollens' reagent and gives iodoform with iodine in alkali.

Compound D does **not** give a silver mirror with Tollens' reagent, but does give iodoform with iodine in alkali.

- * (i) From the results of the experiments, deduce the functional groups present in C and D. By considering the two possible structures for tiglic acid, give the structural formulae of C and D.

From the structures you have drawn, state which of the structures A or B could represent tiglic acid.

Functional group of C is $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ and functional group of D is $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$. and D have Carbonyl group and the Carboxylic group as functional groups respectively.

Structure B represents Tiglic Acid.

- (ii) Explain whether or not these tests show definitely that your answer to (c)(i) represents tiglic acid.

Yes these results represent Tiglic Acid definitely unless no impurities were present. (1)



ResultsPlus
Examiner Comments

Though the formulae are correct there is little attempt to reason.



ResultsPlus
Examiner Tip

Always show your reasoning as fully as possible.

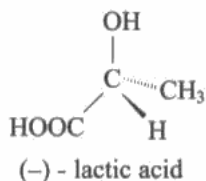
Question 22 (d) (i)

This question was very challenging.

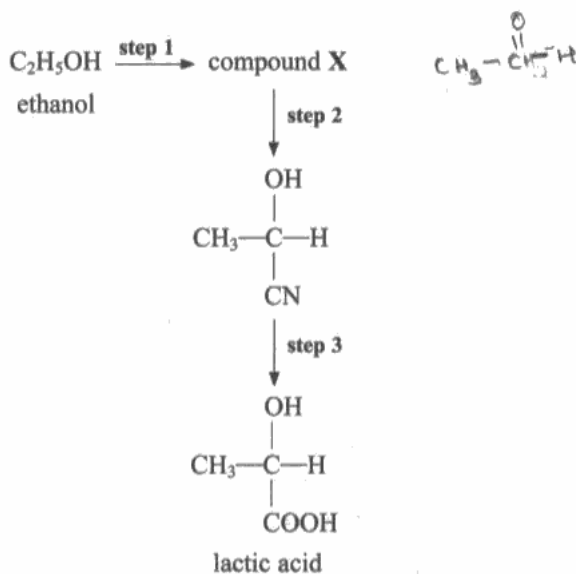
Quite a few could not give the correct intermediate.

The conditions for the two steps were rarely correct, though many know the reagents.

(d) Lactic acid is a chiral molecule that is found in sweat as the (-) isomer only. Its structural formula is

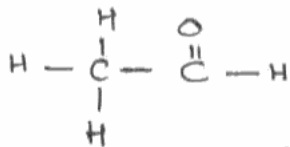


(i) Lactic acid can be made from ethanol in three steps.



Give the structural formula of the intermediate X and the reagents and conditions required for steps 1 and 2.

(4)



Step 1 $\text{H}^+ / \text{K}_2\text{Cr}_2\text{O}_7$

Heat under reflux & allow the product to distil off.

Step 2 HCN

Ethanol & water.



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Examiner Comments

In step 2 if you reflux first a carboxylic acid forms.

KCN is also needed with HCN.

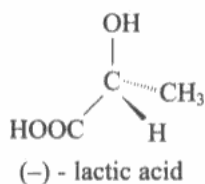


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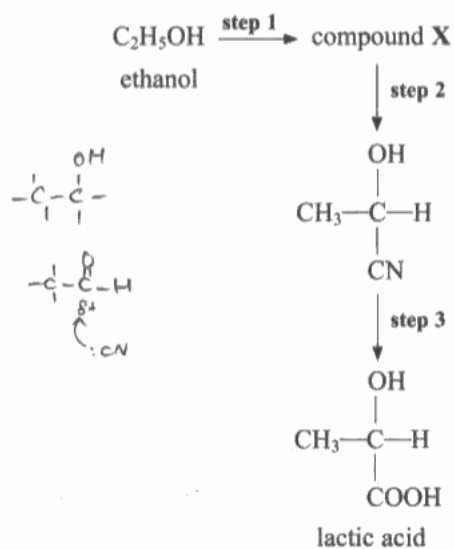
Examiner Tip

This type of question requires the candidate to think about the specific experiment in the question and also the way in which the data will be used to calculate the required value. Avoid vague generalisations!

(d) Lactic acid is a chiral molecule that is found in sweat as the (-) isomer only. Its structural formula is

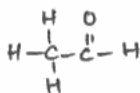


(i) Lactic acid can be made from ethanol in three steps.



Give the structural formula of the intermediate X and the reagents and conditions required for steps 1 and 2.

(4)



Step 1 acidified potassium manganate (VII) and concentrated H_2SO_4 .

Heat under reflux.

Step 2 HCN with catalyst KCN.



ResultsPlus
Examiner Comments

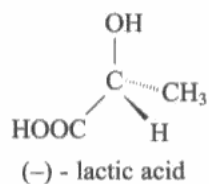
The mixture used in step 2 explodes.



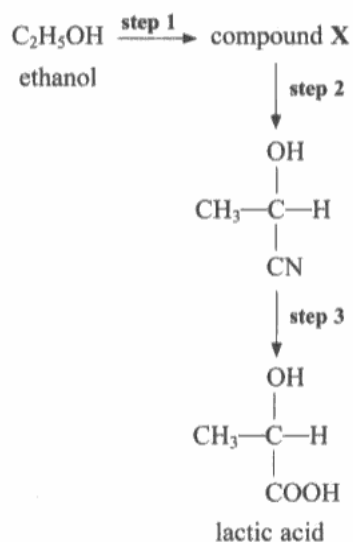
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Examiner Tip

Learn correct chemicals and conditions for organic reactions

(d) Lactic acid is a chiral molecule that is found in sweat as the (-) isomer only. Its structural formula is

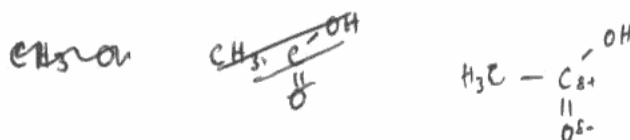


(i) Lactic acid can be made from ethanol in three steps.



Give the structural formula of the intermediate X and the reagents and conditions required for **steps 1** and **2**.

(4)



Step 1 $\text{K}_2\text{Cr}_2\text{O}_7$ in concentrated H_2SO_4 heat under reflux

Step 2 KCN added.



ResultsPlus
Examiner Comments

In step 2 if you reflux, a carboxylic acid forms.

KCN needs to be at pH8



ResultsPlus
Examiner Tip

Learn chemicals and conditions for organic reactions.

Question 22 (d) (ii)

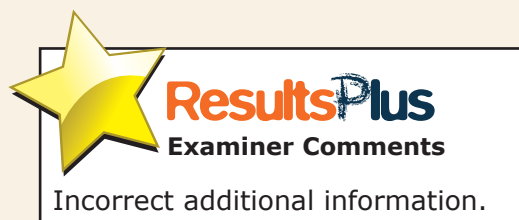
The most common error was to give nucleophilic substitution.

(ii) Classify the type and mechanism of the reaction that occurs in **step 2**. (1)

(Friedel-Crafts reaction) ~~is~~ nucleophilic addition
↳ increasing carbon chain length

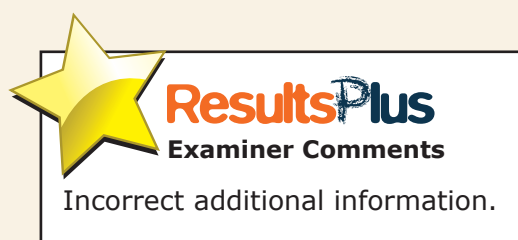
(iii) By considering the stereochemistry of the mechanism in step 2, explain why

edit.



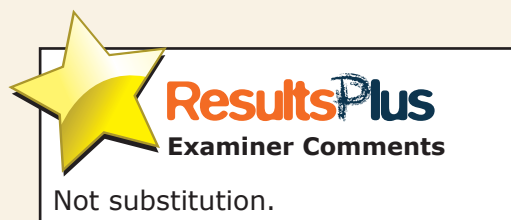
(ii) Classify the type and mechanism of the reaction that occurs in **step 2**. (1)

nucleophilic addition SN² mechanism



(ii) Classify the type and mechanism of the reaction that occurs in **step 2**. (1)

Nucleophilic substitution.



(ii) Classify the type and mechanism of the reaction that occurs in **step 2**.

(1)

electrophilic addition



ResultsPlus
Examiner Comments

Not electrophilic.



ResultsPlus
Examiner Tip

Practise identifying reactions and types.

Question 22 (d) (iii)

The planarity of ethanal at the carbonyl bond was often missed.

The idea of attack from above or below was usually given but often negated by reference to a carbocation indicating confusion with S_N2 .

*(iii) By considering the stereochemistry of the mechanism in **step 2**, explain why this synthesis would **not** give a single optical isomer of lactic acid.

(2)

~~The~~ The nucleophile can attack from above or below ^{of the double bond.} the compound, Thus, forming racemic mixture is obtained.



ResultsPlus Examiner Comments

This scores the mark for attack from above and below but does not mention planarity of the molecule.

*(iii) By considering the stereochemistry of the mechanism in **step 2**, explain why this synthesis would **not** give a single optical isomer of lactic acid.

(2)

The nucleophile attacks the C carbon from either side of the planar.
Thus, racemic mixture formed.



ResultsPlus Examiner Comments

This scores the mark for attack from above and below and nearly gains the second mark but the sentence is incomplete. What is planar?



ResultsPlus Examiner Tip

Always check your answers to make sure they make sense.

Question 22 (d) (iv)

There were many ways of gaining this mark. The most common was by responding that the other stereoisomer may be harmful.

(iv) Suggest why synthetic pathways for the manufacture of pharmaceuticals may require reactions that are highly stereospecific.

(1)

Because ~~diff~~ two optical isomers may have ~~big~~ differences
in their ~~properties~~ properties.



ResultsPlus Examiner Comments

This is insufficient. If the type of properties such as differences in biochemical properties had been mentioned that would have been fine.



ResultsPlus Examiner Tip

Always be as specific as possible, avoid being vague.

(iv) Suggest why synthetic pathways for the manufacture of pharmaceuticals may require reactions that are highly stereospecific.

(1)

To prevent the formation of optical stereoisomers which
will affect the yield ^{and} atom economy.



ResultsPlus Examiner Comments

There were many poor answers like this about yield or atom economy.



ResultsPlus Examiner Tip

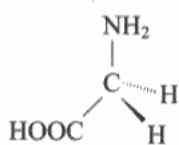
Many saved the day by giving an example of a dangerous stereoisomer like thalidomide.

Question 23 (a) (i-ii)

(i) Weaker candidates gave the non-ionic structure. A displayed formula was accepted on this occasion but this might not always be the case.

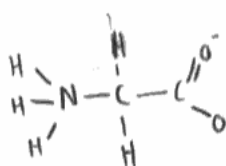
(ii) Few candidates mentioned the high energy needed to break the bonds and few made bonds between molecules clear. Hydrogen bonding was very commonly given.

23 Proteins are polymers of α -amino acids, the simplest of which is glycine.



(a) (i) Draw the **structural** formula for the zwitterion of glycine in the solid state.

(1)



(ii) Explain, on the basis of your answer to (a)(i), why glycine has a relatively high melting temperature for such a small molecule.

(2)

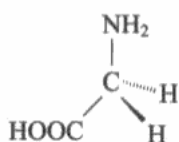
It is enable to form hydrogen bond. Together with the dispersion force and dipole-dipole force, higher melting temperature is needed.



ResultsPlus
Examiner Comments

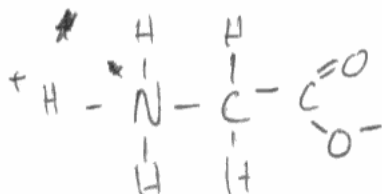
The negative charge in the formula is on the wrong oxygen. No mention of ionic attractions between molecules in (ii).

23 Proteins are polymers of α -amino acids, the simplest of which is glycine.



(a) (i) Draw the **structural** formula for the zwitterion of glycine in the solid state.

(1)



(ii) Explain, on the basis of your answer to (a)(i), why glycine has a relatively high melting temperature for such a small molecule.

(2)

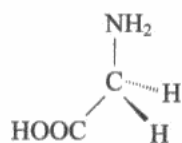
This is because the proton from the COOH group protonates the NH₂ group forming NH₃⁺ and COO⁻, thus the glycine is held together by strong electrostatic forces thus have a high melting point.



ResultsPlus
Examiner Comments

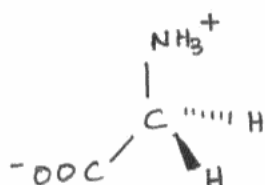
The formula is correct and the ionic forces have been recognised, but it is not clear whether the forces are within molecules, or between molecules.

23 Proteins are polymers of α -amino acids, the simplest of which is glycine.



(a) (i) Draw the **structural** formula for the zwitterion of glycine in the solid state.

(1)



(ii) Explain, on the basis of your answer to (a)(i), why glycine has a relatively high melting temperature for such a small molecule.

(2)

It has both acidic and basic properties and it can form hydrogen bond between two molecules of glycine.



ResultsPlus
Examiner Comments

No mention of ionic attractions between molecules in (ii).

Question 23 (b)

There were various ways of doing this. Most had done thin layer chromatography in one direction, which was fine.

Some described two dimensional chromatography, where different solvents are run at right angles to each other. This was also fine.

Some described column chromatography successfully.

Electrophoresis was not acceptable.

*(b) A solution of hydrolysed protein contains the individual amino acids that make up the protein. Briefly state how you would use chromatography, together with known samples of amino acids, to show which amino acids the protein contained. Do **not** give detailed experimental instructions.

(5)

By using thin layer chromatography the hydrolysed protein solution is dropped onto a paper to form concentrated spot. Other known samples of amino acids are dropped on the same level as the solution. Then put the paper into a solvent and let the solvent run up. Same type of amino acid will stop at same position as the solvent runs up as they have same size. By comparing the position of known samples of amino acids and the protein solution contained exact type of amino acid the protein contained can be identified. Remove the paper before the solvent runs up to the top.



ResultsPlus Examiner Comments

This would have gained full credit if ninhydrin had been mentioned.



ResultsPlus Examiner Tip

It is important to learn details of experiments that you did, and be able to write about them.

* (b) A solution of hydrolysed protein contains the individual amino acids that make up the protein. Briefly state how you would use chromatography, together with known samples of amino acids, to show which amino acids the protein contained. Do not give detailed experimental instructions.

(5)

Do the process of chromatography, which gives
coloured spots when sprayed with ninhydrin.

Record the results with the colour ~~that~~ seen.

Compare with the data values of known amino acids.

If the values and colour are closely related,

then the result can be considered as valid.



ResultsPlus

Examiner Comments

This would have scored a second mark if the data compared had been specified as R_f values.

Question 24 (a) (i)

Most realised that it was because the structure of the molecule was not known.

(a) (i) Explain why Perkin's attempted synthesis of quinine was almost certain to fail.

(1)

because he did not know the structure of benzene, hence he would not know how the benzene would react to chemical reactions.



ResultsPlus

Examiner Comments

A common misconception. Though it is true, it is not enough, to synthesize quinine its full structure needed to be known.



ResultsPlus

Examiner Tip

With this type of question it is important to read the passage carefully - the answer was clearly there.

Question 24 (a) (ii)

Very few candidates gained credit here. Most thought that India and/or Holland became more affluent, without considering the reasons.

(ii) Suggest the effect that the growth of the organic chemicals industry in the late 19th century had on Holland and India in particular.

(2)

Synthetic dyes were made available in large quantities.
and it was cheaper source than using plants.



ResultsPlus

Examiner Comments

This gains the first mark for cheaper sources available but only answers part of the question. It does not address its effect on the farmers in India and Holland.



ResultsPlus

Examiner Tip

Read the passage carefully, then consider its implications when asked.

(ii) Suggest the effect that the growth of the organic chemicals industry in the late 19th century had on Holland and India in particular.

(2)

This would have increased the export from both
India and Holland and would have increased
the economical growth. The economy in India
would have grown.



ResultsPlus

Examiner Comments

This fails to address either marking point. There is no mention of cheaper alternatives and the effect on growers is ignored.

Question 24 (b) (i)

It was important to read that an observation, something you would see, was needed. Then it was necessary to see the significance of this for the proposed structure.

(b) (i) What observation did Kekulé make to show that benzene does **not** react with bromine water? Explain the significance of this with reference to his representation of the molecule.

(2)

Benzene didn't decolourise bromine water.



ResultsPlus

Examiner Comments

The second part of the question has not been answered.



ResultsPlus

Examiner Tip

RTQ² Read the question twice.

(b) (i) What observation did Kekulé make to show that benzene does **not** react with bromine water? Explain the significance of this with reference to his representation of the molecule.

(2)

The enthalpy change of hydrogenation is ~~more~~ ^{less} negative. i.e. -250 kJ mol^{-1} rather than -360 kJ mol^{-1}



ResultsPlus

Examiner Comments

The key words 'What observation...' and 'Explain the significance ...' were not underlined and probably ignored, so the candidate has gone off on entirely the wrong track.



ResultsPlus

Examiner Tip

Read the question twice.

Question 24 (b) (ii)

'Benzene is more stable because six carbon p-electrons are delocalised round the ring' is a simple way of gaining full credit. The mark for delocalisation of electrons was most commonly awarded. The stability mark was next most common, though it was often negated by contradictory statements like less energy required to break bonds.

(ii) Explain, in terms of the bonding in the benzene ring, why the enthalpy of hydrogenation is less exothermic than would be expected from a molecule with three double bonds.

(3)

Some of the energy is already used in the delocalization of electrons. The double bond keeps on shifting which makes it electron attracting in nature and thus more reactive so the enthalpy of hydrogenation is less exothermic.



ResultsPlus

Examiner Comments

While this gains credit for 'the delocalisation of electrons', it misses out on the stability mark due to the lack of understanding of energy which was quite a common problem. The molecule is more stable so it is less reactive, with a less negative enthalpy of hydrogenation. Energy is not used to delocalise electrons.

(ii) Explain, in terms of the bonding in the benzene ring, why the enthalpy of hydrogenation is less exothermic than would be expected from a molecule with three double bonds.

(3)

A molecule with 3 ~~double~~ ^{double} bonds a value of -360 kJ mol^{-1} (for C_6H_6)
in the enthalpy ^{change} of hydrogenation. In reality benzene gives -205 kJ mol^{-1} . The 155 kJ mol^{-1} difference is the resonance energy. This energy is the result of the increased stability promoted by the delocalised system of electrons in benzene. The 155 kJ mol^{-1} enthalpy of hydrogenation is less exothermic as the benzene molecule is already stabilised by 155 kJ mol^{-1} ^{than} the respective Kekulé structure.



ResultsPlus

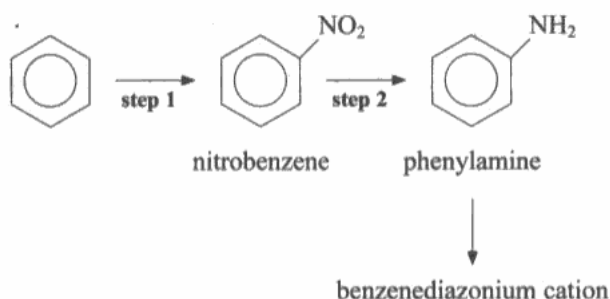
Examiner Comments

This answer recognises the stability of benzene due to its delocalised electrons, but fails to mention which electrons are delocalised.

Question 24 (c)

Many careful candidates gained full credit here. Careless errors were the omission of charges in the equation for the formation of the nitronium ion, arrows drawn too loosely, and protons disappearing in the final step.

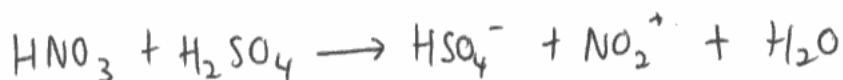
(c) The first steps in the preparation of an azo dye from benzene are shown below.



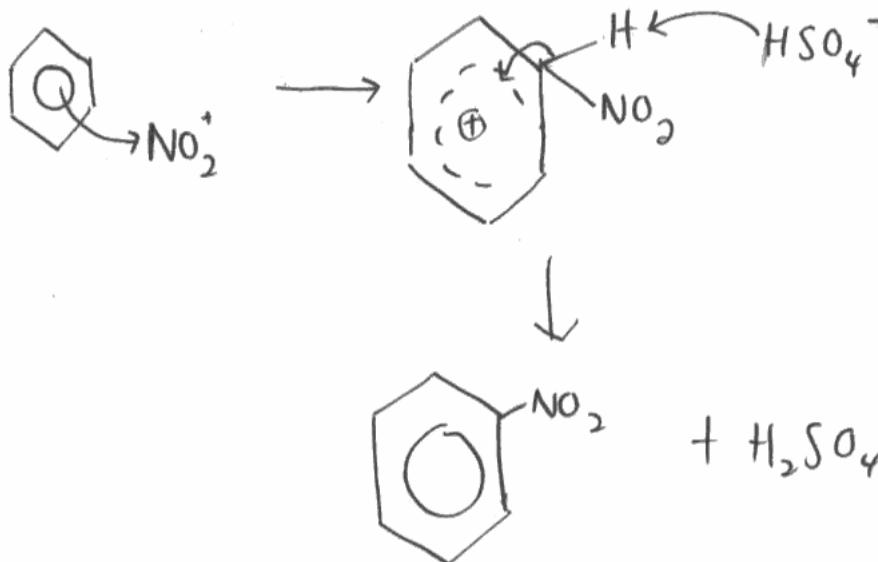
Give the mechanism for the reaction in **step 1**, including the equation for the formation of the electrophile.

(4)

Equation for formation of electrophile



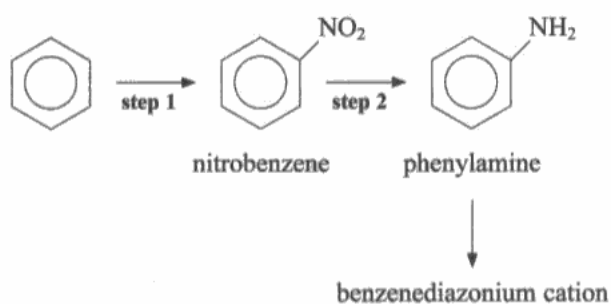
Mechanism



ResultsPlus
Examiner Comments

The only problem here is the full dashed line around the inside of the benzene ring in the intermediate state. It should of course go around all the atoms except the carbon with four bonds.

(c) The first steps in the preparation of an azo dye from benzene are shown below.



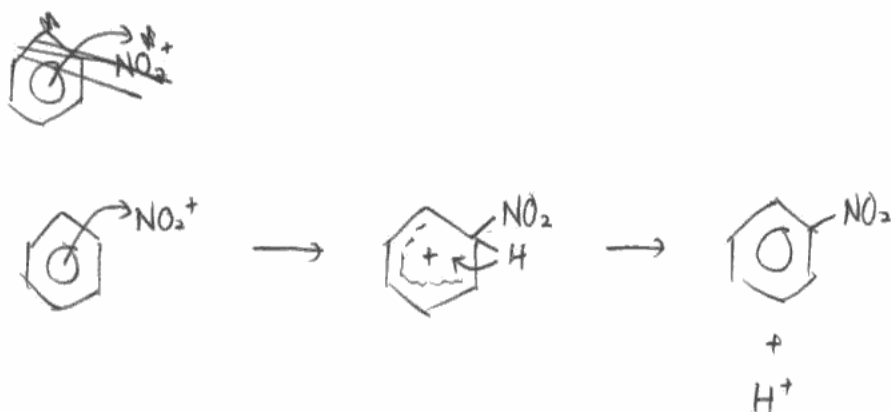
Give the mechanism for the reaction in **step 1**, including the equation for the formation of the electrophile.

(4)

Equation for formation of electrophile



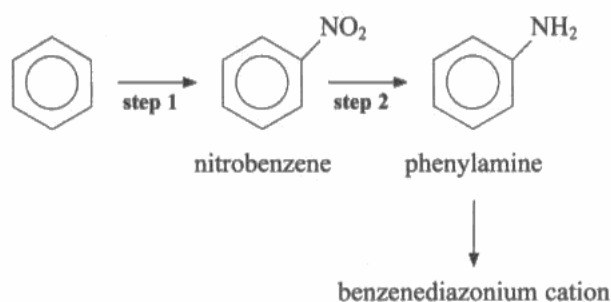
Mechanism



ResultsPlus
Examiner Comments

This is fine except that the arrow in the final step should go from the C-H bond into the benzene ring, rather than from the hydrogen.

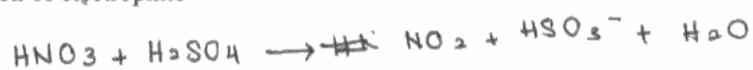
(c) The first steps in the preparation of an azo dye from benzene are shown below.



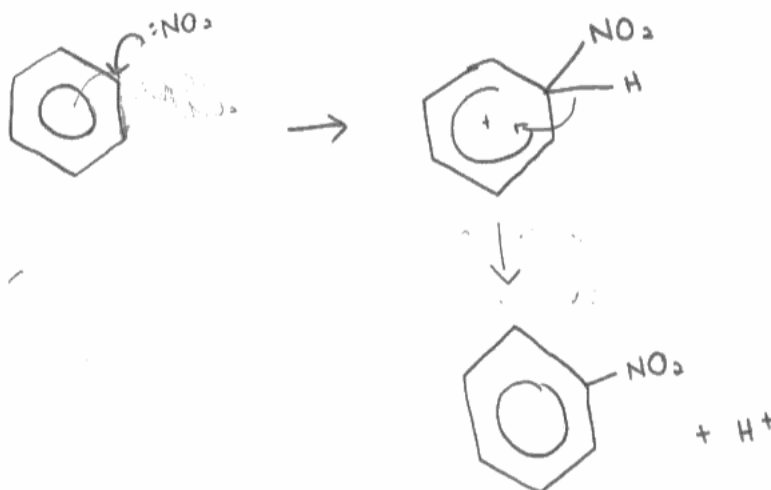
Give the mechanism for the reaction in **step 1**, including the equation for the formation of the electrophile.

(4)

Equation for formation of electrophile



Mechanism



ResultsPlus
Examiner Comments

This has several errors. First an oxygen is lost in the equation where an HSO_3^- ion is formed and a charge is missing from the NO_2^+ . Second the arrow in step 1 should go from the ring to the attacking group



ResultsPlus
Examiner Tip

Learn the detail of electrophilic aromatic substitution thoroughly.

Question 24 (d) (i)

It was necessary to consider both higher and lower temperatures. Then specific statements were needed.

- (d) (i) Phenylamine is converted into the benzenediazonium cation using sodium nitrite and hydrochloric acid at a temperature between 0 °C and 10 °C.

Explain why the temperature must **not** be lower or higher than these limits if a good yield is to be obtained.

(2)

Any lower and the reaction will be too slow as there won't be enough kinetic energy in the molecules. Any higher and secondary reactions will start to take place forming different products.



ResultsPlus
Examiner Comments

The first point is fine, the reaction would be too slow. The second is too vague.

- (d) (i) Phenylamine is converted into the benzenediazonium cation using sodium nitrite and hydrochloric acid at a temperature between 0 °C and 10 °C.

Explain why the temperature must **not** be lower or higher than these limits if a good yield is to be obtained.

(2)

Or else, a phenol or an alcohol will be formed, which are unwanted products. A temperature of 0°C to 10°C should be maintained to prevent any unwanted products to be formed, thereby increasing the yield.



ResultsPlus
Examiner Comments

This does not make it clear when phenol forms. It does at higher temperatures than 10 °C.

- (d) (i) Phenylamine is converted into the benzenediazonium cation using sodium nitrite and hydrochloric acid at a temperature between 0 °C and 10 °C.

Explain why the temperature must **not** be lower or higher than these limits if a good yield is to be obtained.

(2)

* Diazonium compounds easily ~~dissociate~~ decompose
so increasing the temperature beyond 10° would
result in no products because the products
would have ~~dissociated~~ decomposed.



ResultsPlus Examiner Comments

Though a little convoluted, this response gains the second mark for the diazonium compound decomposing at higher temperatures. Unfortunately lower temperatures are not considered.



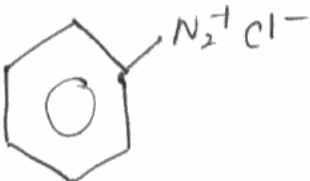
ResultsPlus Examiner Tip

Always read the last line of a question particularly carefully.

Question 24 (d) (ii)

This was marked generously on charge position and on the benzene ring, where C-H bonds were not required.

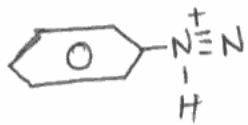
(ii) Draw the structural formula of the benzenediazonium cation showing all the bonds and the charge. (1)



ResultsPlus
Examiner Comments

The bonds have not been shown as requested in the question

(ii) Draw the structural formula of the benzenediazonium cation showing all the bonds and the charge. (1)



ResultsPlus
Examiner Comments

Five bonds to a nitrogen never happen. Remove the hydrogen and this is fine.

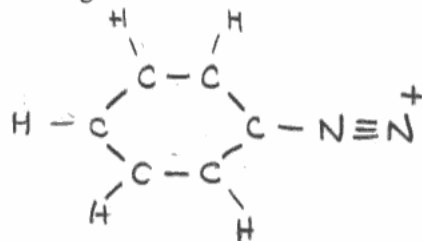


ResultsPlus
Examiner Tip

Nitrogen forms three bonds, or four bonds if it is positively charged.

(ii) Draw the structural formula of the benzenediazonium cation showing all the bonds and the charge.

(1)



ResultsPlus
Examiner Comments

A very good displayed formula but for one thing – the ring representing the delocalised bond is omitted.



ResultsPlus
Examiner Tip

There are normally four bonds made to each carbon.

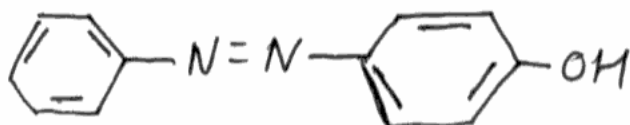
Question 24 (d) (iii)

Many used phenol, though probably used 2-naphthol in their class experiments. With phenol two benzene rings joined by N=N were needed, then an OH which could be in any position on a benzene ring.

(iii) Suggest how you could convert a sample of the benzenediazonium cation into an azo dye. Give the name of the other compound you would use and the skeletal formula of the azo dye you would obtain.

(3)

Name of the other compound: phenol



ResultsPlus
Examiner Comments

Structures involving alternating double and single bonds in the rings were fine, so this gains two marks. The phenol needs to be dissolved in sodium hydroxide.



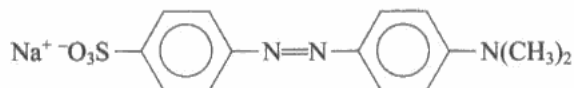
ResultsPlus
Examiner Tip

Learn all details of chemicals used in experiments.

Question 24 (e)

The two marks and the question asking for the main features showed that two points were required. Many only gave one, usually the first about the potential of oxygen and nitrogen to hydrogen bond.

(e) The structural formula of methyl orange is given below.



Suggest the main features of methyl orange which make it water-soluble, giving your reasons.

(2)

It forms hydrogen bonds with water. It has some

It contains electronegative elements that enable it to

form effective hydrogen bonds with water.

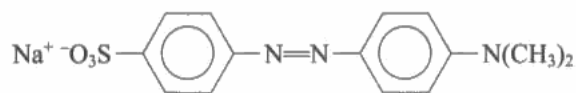
(Total for Question 24 = 20 marks)



ResultsPlus
Examiner Comments

This answer needs to specify the actual elements in the compound which can hydrogen bond with water to gain the first mark. There is no mention of the interaction of the negative charge on the sulfonate group and the slightly positive hydrogen atoms in water.

(e) The structural formula of methyl orange is given below.



Suggest the main features of methyl orange which make it water-soluble, giving your reasons.

(2)

The charges on Na⁺ and -O₃S⁻ causes them to be hydrated by water molecules when mixed with water. The energy liberated is high enough to overcome the dissolving the compound.

(Total for Question 24 = 20 marks)



ResultsPlus

Examiner Comments

This gains the second mark but fails to mention hydrogen bonding with N or O in the compound for the first mark.



ResultsPlus

Examiner Tip

In questions on solubility consider all possibilities that help to make compounds soluble.

Paper Summary

Many good candidates were solid on the organic chemistry questions but found some of the physical chemistry questions more difficult, especially those involving electrode potentials. Most of the inorganic chemistry questions seemed to be answered correctly.

There were the usual issues with quality of written communication.

The word molecule was often used instead of attached group when writing about attached groups in molecular structures.

The terms molecule, atom and ion were also confused.

Hydration and hydrolysis were often confused, as were hydration and hydrogenation.

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