edexcel

Edexcel GCE

Chemistry
6245/01

June 2006

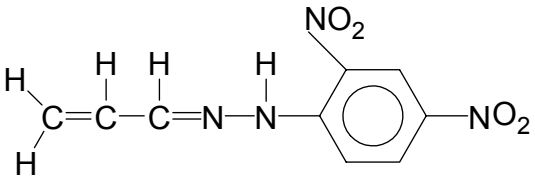
advancing learning, changing live

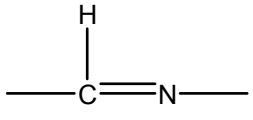
Results Mark Scheme

Edexcel GCE
Chemistry
6245/01

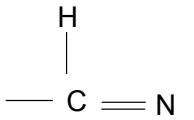
1. (a) (i) Yellow/orange precipitate (allow red/any shades of red) **(1 mark)**

(ii)





(1)



Must be formed by C atom from the C = O group

(2 marks)

rest of molecule correct **(1)**

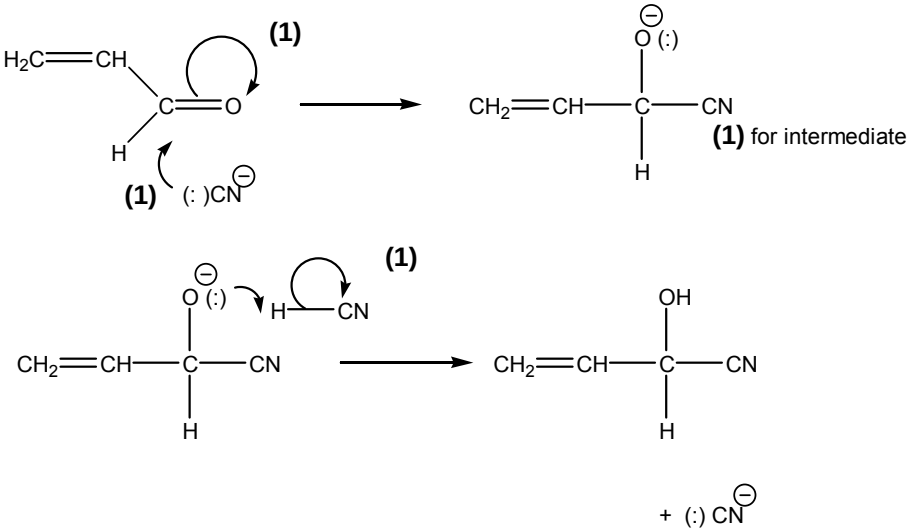
(b) Hydrogen nuclei OR hydrogen atoms OR hydrogen(s) OR protons **(1)**

in (three) different environments (may be shown by diagram) **(1)**

Ratio 2:1:1 **(1)** **(3 marks)**

Any reference to fragments or bonds scores zero

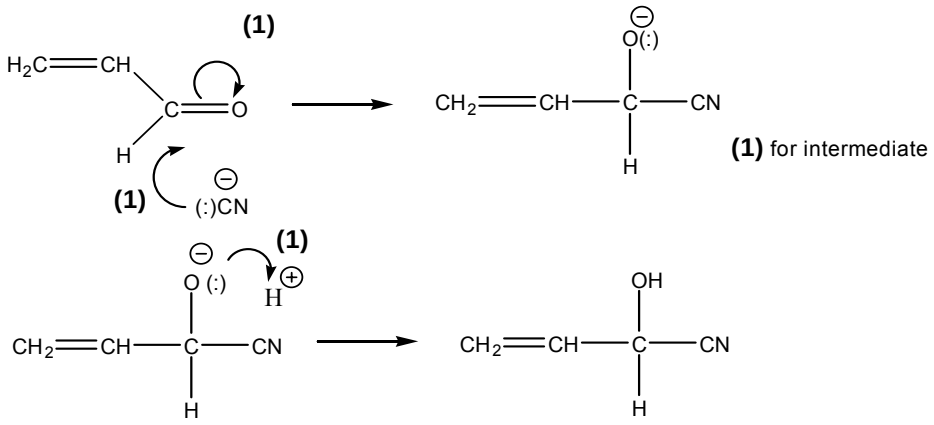
(c) (i) EITHER



Lone pairs not essential.
Arrow may start from minus of O

- The intermediate is not consequential on their first step
- The minus of the cyanide ion can be on either the C or the N
- The arrow can start from the minus of $^{-}$CN in step 1 (but not from the minus of CN^{-}) and can start from the minus of O^{-} in step 2
- The arrow from the bond must not go past the O atom
- Lone pairs not essential
- Single step addition of HCN scores zero
- Autoionisation of C=O can only score the last two marks
  ie max 2

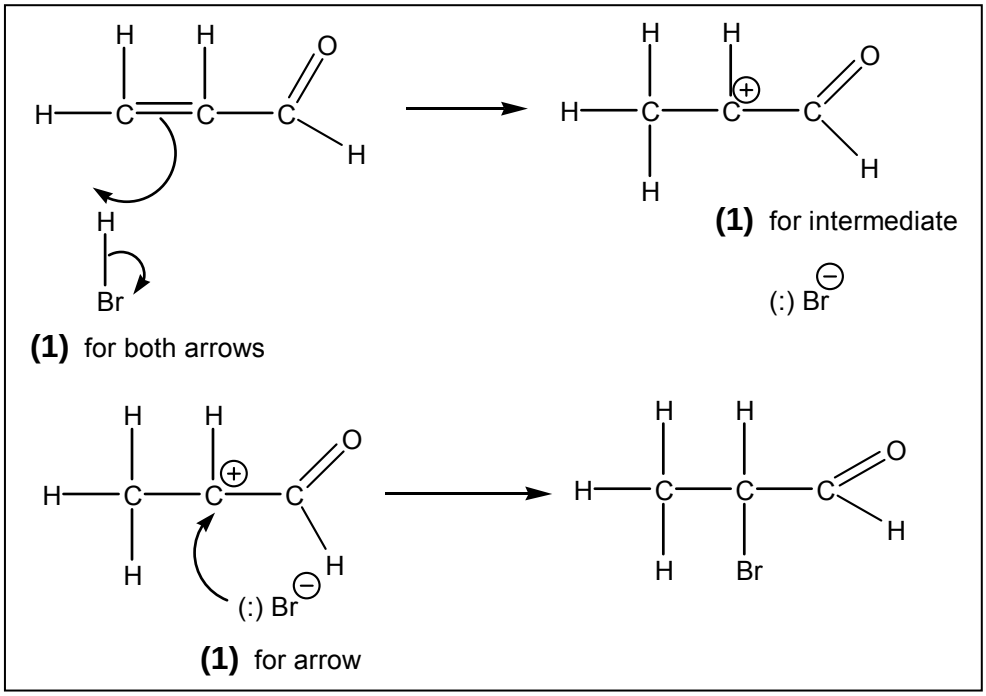
OR



- The intermediate is not consequential on their first step
- The minus of the cyanide ion can be on either the C or the N
- The arrow can start from the minus of ^{-}CN in step 1 (but not from the minus of CN^{-}) and can start from the minus of O^{-} in step 2 **(4 marks)**
- The arrow from the bond must not go past the O atom
- Lone pairs not essential
- Single step addition of HCN scores zero
- Autoionisation of C=O can only score the last two marks ie max 2

(ii) Nucleophilic addition **(1 mark)**
Stand alone

(d) (i)



(3 marks)

Note: If Br is on the wrong carbon atom, only third mark available

(ii) Electrophilic addition **(1 mark)**
Stand alone

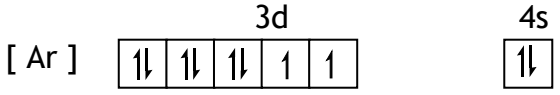
(e) QWC*

- C = O is a polar bond OR O more electronegative than C **(1)**
- C = C has high electron density OR C = C is electron rich **(1)**
  IGNORE "C=C is non-polar" *and* references to π bond
- $C^{\delta+}$ can be attacked by a nucleophile OR (C in) C = O can be attacked by nucleophile
  OR C = C attacked by electrophile **(1)**

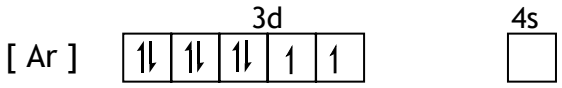
(3 marks)

Total for question: 18 marks

2 (a)



(1)



(1) **(2 marks)**

Allow ↑ instead of 1 and ↓ instead of ↿

(b) Forms **ion(s)** which have a partially OR an incompletely filled *d*-(sub)shell OR *d*-orbital(s) **(1 mark)**

(c) (i) Dative (covalent) OR co-ordinate **(1)**

Covalent **(1)** **(2 marks)**

(ii) $[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Ni(OH)_2(H_2O)_4] + 2NH_4^+$

OR

$[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow Ni(OH)_2 + 4H_2O + 2NH_4^+$

OR

$[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow [Ni(OH)_2(H_2O)_4] + 2H_2O$

OR

$[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + 6H_2O$

IGNORE state symbols

IGNORE missing square brackets in any formula **(1 mark)**

(iii) H^+ removed (by NH_3 OR OH^-)**(1)**

From (H_2O) **ligands (1)** **(2 marks)**

NOT just from "complex"

(iv) Ligand exchange
OR ligand replacement
OR ligand substitution **(1 mark)**

(v) $[Ni(OH)_2(H_2O)_4] + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 2OH^- + 4H_2O$

OR

$Ni(OH)_2 + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 2OH^-$

Allow formation of $[Ni(NH_3)_4]^{2+}$ OR $[Ni(NH_3)_4(H_2O)_2]^{2+}$

cation formed **(1)**

balancing equation **(1)** **(2 marks)**

(d) *d*-orbital**s** split (in energy) by ligands **(1)**
QWC* ALLOW d-sublevel

absorbs light (in visible region) **(1)**
NOT "uv light"

electron is promoted OR electron moves to a **higher** energy level **(1)** **(3 marks)**

Any mention of emission of light can only score 1st mark

Total for question: 14 marks

3 (a) Rate of decrease OR rate of change in **concentration** of reactants
OR rate of increase OR rate of change in **concentration** of products.
OR change in **concentration** of reactants with time OR change in **concentration** of products with time **(1)**
NOT just 'amount'
Sum of the **powers** to which the **concentrations** are raised in **the rate equation** OR number of species involved in (up to and including) the rate determining step OR sum of partial orders **if** illustrated with a general rate equation **(1)**
'Sum of the partial orders' alone does not score. **(2 marks)**

(b) (i) Both orders correct **(1)**

EITHER
Expt 1 + 3: double [A], doubles rate so order **1** **(1)**
Expt 1 + 2: double [B], four x rate so order **2** **(1)**
OR
Double [A] keeping [B] constant doubles rate so order **1** **(1)**
Double [B] keeping [A] constant four x rate so order **2** **(1)** **(3 marks)**
Omission of experiment number or keeping a concentration constant to be penalised ONCE only **(1)**

(ii) Rate = k [A] $[B]^2$.
Mark consequentially on (i) **(1 mark)**

(iii) $k = \frac{\text{rate}}{[A]\ [B]^2} = \frac{0.00200}{0.100 \times (0.100)^2}$

$= 2(.00)$ **(1)** $mol^{-2}\ dm^6$ **min^{-1}** **(1)**

Consequential on their rate equation in (ii)
Use of experiment 2 or experiment 3 can score max **(1)** **(2 marks)**

(iv)

$A + B \rightarrow AB$
$AB + B \overset{rds}{\rightarrow} AB_2$
} **(1)** *for first two equations*

$AB_2 + B \overset{fast}{\rightarrow} AB_3$ **(1)**

OR

$B + B \rightarrow B_2$
$A + B_2 \overset{rds}{\rightarrow} AB_2$
} **(1)** *for first two equations*

$AB_2 + B \overset{fast}{\rightarrow} AB_3$ **(1)**

OR

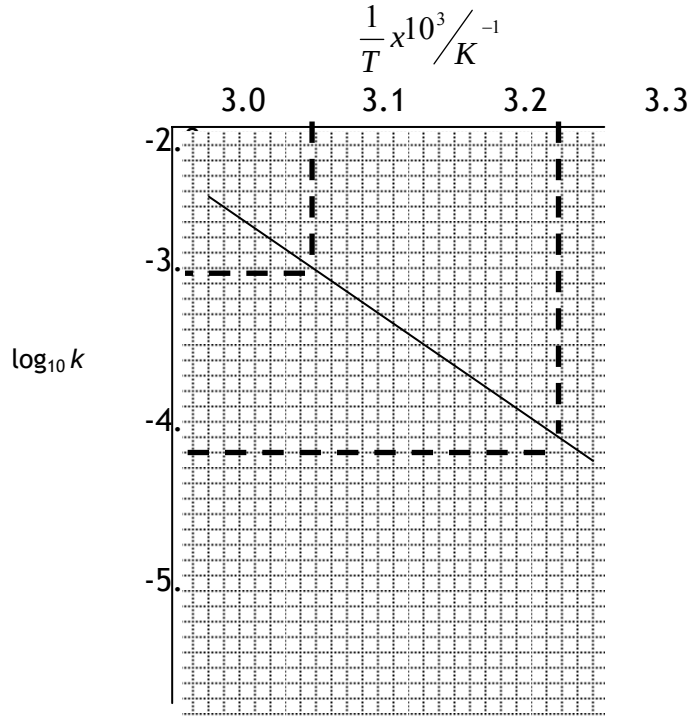
$A + 2B \overset{slow\ /\ rds}{\rightarrow} AB_2$ **(1)**

$AB_2 + B \overset{fast}{\rightarrow} AB_3$ **(1)**

Identifying slow(est) OR rate determining step by appropriate notation **(1)** **(3 marks)**

S_N1 or S_N2 scores zero

(c) (i)



All points plotted accurately **(1)**
with best-fit straight line drawn **(1)** **(2 marks)**

(ii)

Gradient eg = $\frac{-4.25-(-3.10)}{0.00330-0.00310}$

= $\frac{-1.15}{0.00020}$

= **-**5750 (K) **(1)**

ALLOW = -5450 to -6050 (K) but MUST have a negative sign
ALLOW if gradient is left as a correct fraction such as -$\frac{1.15}{0.00020}$

E_a = (+)5750 x 2.30 x 8.31

= (+)110 kJ mol^{-1} / (+) 110000 J mol^{-1} **(1)**

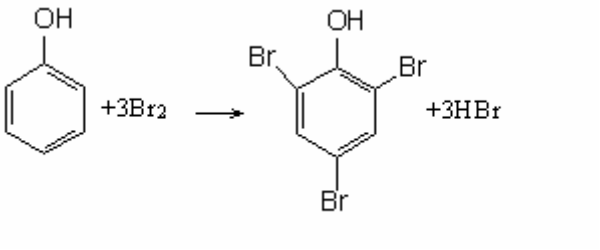
ALLOW = (+)104 to (+)116 kJ mol^{-1}

IGNORE S.F. **(2 marks)**

(2nd mark consequential on gradient, but value of E_a must be in correct units)

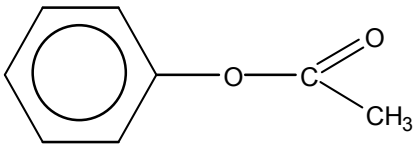
Total for question: 15 marks

4 (a) (i) White precipitate OR white suspension OR white solid **(1 mark)**

(ii) 

2,4,6-tribromophenol **(1)**
rest of equation if for formation of a tribromophenol **(1)**

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$ scores **(1)** **(2 marks)**

(iii) 

(1 mark)

C = O in ester must be shown

(iv) C (atom) is (very) δ+ because **Cl** highly electronegative OR Cl electron withdrawing **(1)**
IGNORE references to oxygen

(so C atom) susceptible to nucleophilic attack OR (so C atom) strongly electrophilic **(1)** **(2 marks)**
IGNORE references to activation energy

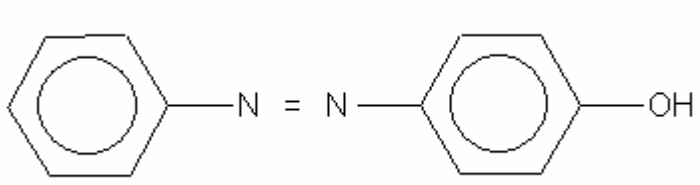
(b) Sn **and** **conc** hydrochloric acid (accept conc HCl) OR Fe **and** **conc** hydrochloric acid (accept conc HCl) **(1 mark)**
IGNORE any references to NaOH
IGNORE references to Fe or Sn as a catalyst

(c) (i)
- Sodium nitrite OR $NaNO_2$ OR sodium nitrate(**III**) **(1)**
  NOT JUST HNO_2
- Hydrochloric acid OR dilute sulphuric acid OR aqueous sulphuric acid

ACCEPT HCl if qualified. Do not accept conc. sulphuric acid **(2 marks)**
Only award the hydrochloric acid mark if $NaNO_2$ or KNO_2 or HNO_2 given as co-reagent

(ii) Below 0°C : reaction too slow **(1)**

Above 5°C : product decomposes OR diazonium ion decomposes **(1)** **(2 marks)**
NOT HNO_2 decomposes

(iii) 

OR $-O^-$ instead of –OH group **(1 mark)**

(iv) QWC*

Dissolve in **minimum** volume of boiling solvent OR dissolve in **minimum** volume of hot solvent **(1)**

NOT JUST "small volume"

[*ALLOW* any specified solvent including water]

Filter **hot** OR filter through **heated** funnel **(1)**

Cool or leave to crystallise **(1)**

Filter (under suction) **(1)**

Wash solid with cold solvent (and leave to dry)

OR wash solid with small volume of solvent (and leave to dry) **(1)**

(5 marks)

Total for question: 17 marks

5 (a) (i) **EITHER**

ΔE^{θ} = (+) 0.15 (V) OR E^{θ} (MnO_4^- / Mn^{2+}) more positive or greater than E^{θ} (Cl_2/ Cl^-); accept reverse argument **(1)**
(so) MnO_4^- reacts with Cl^- OR Cl^- ions form Cl_2
OR $KMnO_4$ reacts with HCl **(1)**
OR
$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$ **(1)**
E^{θ} = (+) 0.15(V) **(1)**

(2 marks)

(ii) stated colour change of colourless to (pale) pink NOT purple OR stays (pale) pink
OR pink to colourless
OR first excess of (coloured) manganate((VII))
IGNORE "self-indicating" **(1 mark)**
IGNORE references to Mn^{2+}

(b) (i) (Multiply iron half-equation by five to) cancel out electrons OR balance electrons **(1 mark)**

(ii)

Moles MnO_4^- = $\frac{0.0200 \times 20.10}{1000}$

= 0.000402 mol MnO_4^- **(1)**

Moles Fe^{2+} per 25.0 cm^3 = 5 x 0.000402
= 0.00201 mol Fe^{2+} **(1)**

Moles Fe^{2+} per 200 cm^3 = $0.00201 \times \frac{200}{25}$ mol Fe^{2+}
= 0.01608 mol Fe^{2+} **(1)**

Mass of $FeSO_4 . 7H_2O$ = 0.01608 x 278
= 4.47g or via concentrations **(1)**

Percentage purity = $\frac{4.47}{6.00} \times 100\%$
= 74.5% **(1)** *ALLOW* 74.7% / 75%

Correct answer + working **(5)**
ALLOW 2 or more sig figs
If start by dividing $\frac{6.00}{278}$, and final answer is **incorrect**, candidate can access first three marks only.

(5 marks)

If third step omitted, answer 9.3% OR 9.33% OR 9.4%

(c) (i) E^{θ} = + 1.46 - (- 0.13) = (+) **1.59** (V) **(1 mark)**
Correct answer alone **(1)**

(ii) $PbSO_4$ precipitated **(1)**
$[H^+_{(aq)}]$ not 1 mol dm^{-3} **(1)**
$[Pb^{2+}_{(aq)}]$ not 1 mol dm^{-3} **(1)**
} *any one of these*
the conditions (in the car battery) are not standard **(1)** **(1 mark)**
" temperature non-standard" alone or "not 1 atm pressure" alone does not score

Total for question: 11 marks

Total for paper: 75 marks