A competition to select the team to represent the

UNITED KINGDOM

at the

XXXVIIth INTERNATIONAL CHEMISTRY OLYMPIAD

ANSWER BOOKLET FOR MARKERS

Round I - 2005

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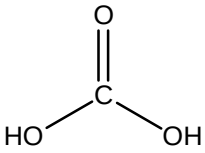
Olympiad Round 1 2005 – Mark Scheme

1. This question is about carbon oxides

(a) i) $CaCO_{3\,(s)} + 2HCl_{\,(aq)} \longrightarrow Ca^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)} + H_2O + CO_{2\,(g)}$
(state symbols not required; $CaCl_2$ also fine) **(1)**

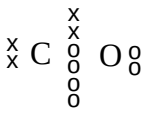
ii)



(1)

(b) i) $HCOOH + H_2SO_4 \longrightarrow CO_{\,(g)} + H_2O + H_2SO_4$ **(1)**

ii)

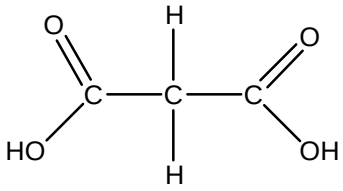


(1)

iii) TRIPLE bond **(1)**

(c) i) $Pd^{2+}{}_{(aq)} + CO + H_2O \longrightarrow CO_{2\,(g)} + Pd_{\,(s)} + 2H^{+}{}_{(aq)}$ **(1)**

(d) i)

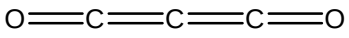


propan-1,3-dioic acid

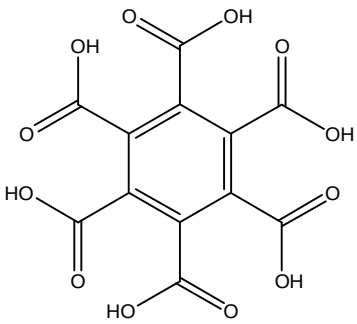
$C_3H_4O_4 \longrightarrow 2H_2O + C_3O_2$

(2)

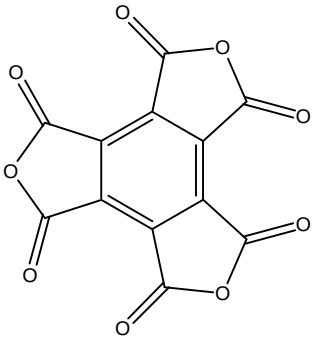
ii) **(1)**



(e)



benzene hexacarboxylic acid



$C_{12}O_9$

(2)

Total: 11

2. This question is about diiodine pentoxide

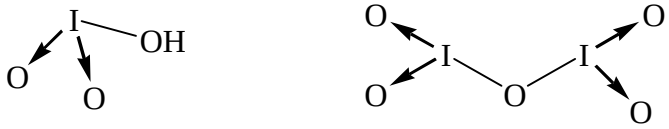
(a) $I_2O_5 + 5\ CO \rightarrow I_2 + 5\ CO_2$ **(1)**

(b) Amount of $S_2O_3^{2-} = 8.00\ cm^3 \times 0.100\ mol\ dm^{-3} = 8.00 \times 10^{-4}$ mol
$\therefore$ Amount of $I_2 = 4.00 \times 10^{-4}$ mol
$\therefore$ Amount of $CO = 2.00 \times 10^{-3}$ mol
$\therefore$ Volume of $CO = 2.00 \times 10^{-3}\ mol \times 24\ dm^3\ mol^{-1} = 48\ cm^3$
$\therefore$ Percentage by volume of $CO = 48\ cm^3/150\ cm^3 \times 100\% = 32\%$ **(2)**

(c) Molar mass of $I_2O_5 = (2\times126.90\ g\ mol^{-1}) + (5\times16.00\ g\ mol^{-1}) = 333.80\ g\ mol^{-1}$.
To form 1 mol of I_2O_5, mass of anhydride required
= 333.80 g / (1-0.01766) = 339.80 g.
The mass loss of (339.80 - 333.80 = 6.00) g is equivalent to 1/3 of a mole of water, so 3 moles of I_2O_5 must be produced for each mole of water eliminated, making the equation $H_2I_6O_{16} \rightarrow 3\ I_2O_5 + H_2O$
The empirical formula of the parent acid is therefore HI_3O_8.
(It is actually $HIO_3.I_2O_5$.) The equation for the dehydration is:
$2\ HI_3O_8 \rightarrow 3\ I_2O_5 + H_2O$ **(2)**

(d) Parent acid: HIO_3.
Equation for formation is: $I_2O_5 + H_2O \rightarrow 2\ HIO_3$
Oxidation state of iodine in I_2O_5: +5 **(2)**

(e)



Accept chemically sensible alternatives. **(2)**

(f) $I_2 + 5\ Cl_2 + 6\ H_2O \rightarrow 2\ HIO_3 + 10\ HCl$
(Appreciation that chlorine is oxidising iodine up to its +V oxidation state, and itself being reduced to chloride reveals the I_2:Cl_2 stoichiometry. The other numbers follow straightforwardly.) **(1)**

Total: 10

3. This question is about ants

(a) i)) $6.0 \times 10^{-3} \times 0.5 \times 100 / 80 = 3.75 \times 10^{-3}$ cm^3 so accept 3.8×10^{-3} cm^3

ii) $1000 / 3.75 \times 10^{-3} = 2.7 \times 10^5$

(b) i) $HCOOH + NaHCO_3$? $HCOONa + H_2O + CO_2$

ii) $6.0 \times 10^{-3} \times 0.5 \times 1.2 / 46 = 7.8 \times 10^{-5}$ moles

iii) $7.8 \times 10^{-5} \times 84 = 6.6 \times 10^{-3}$ g = 6.6 mg

(c) 7.8×10^{-2} mol dm^{-3}

(d) 3.7×10^{-3} mol dm^{-3}

(e) $3.7 \times 10^{-3} / 7.8 \times 10^{-2} \times 100 = 4.8$ %

(f) $(3.7 \times 10^{-3})^2 / (7.8 \times 10^{-2} - 3.7 \times 10^{-3}) = 1.8 \times 10^{-4}$ mol dm^{-3} (also accept 1.9×10^{-4}). This means $pK_a = 3.73$.

1 mark for each part

Total: 9

4. This question is about the NMR spectra of NanoPutians

(a) 6 ≡ 8, 9 ≡ 11, 19 ≡ 23, 20 ≡ 22
8 signals in total due to benzene ring carbons **(2)**

(b) 4 ≡ 13, 5 ≡ 12, 24 ≡ 30, 25 ≡ 31
4 signals in total due to triple bond carbons **(2)**

(c) 1 ≡ 16, 27 ≡ 28 ≡ 29 ≡ 33 ≡ 34 ≡ 35, 40 (unique), 41 (unique)
4 signals in total due to methyl group carbons **(3)**

(d) 23 different environments (i.e. **23** different signals)
(2 marks for the correct answer. 1 if the answer given is 22)

(e) signal split into **6**, ratio 1**: 5 : 10 : 10 : 5 : 1** **(1)**

(f)

^{1}**H NMR Signal**	**Hydrogen(s) on Carbon(s)**
A	7
B	**19, 23**
C	9, 11
D	36
E	17
F	37 and 39
G	37 and 39
H	3, 14
I	2, 15
J	40 or 41
K	27, 28, 29, 33, 34, 35
L	1, 16
M	41 or 40

(6)

Total: 16

5. This question is about the Breathalyser

(a) i) $CH_3CH_2OH + H_2O$? $CH_3CO_2H + 4H^+ + 4e^-$ **(1)**

ii) $Cr_2O_7^{2-} + 6e^- + 14H^+$? $2Cr^{3+} + 7H_2O$ **(1)**

iii) $3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+$? $3CH_3CO_2H + 4Cr^{3+} + 11H_2O$ **(2)**

iv) $3CH_3CH_2OH + 2K_2Cr_2O_7 + 8H_2SO_4$? $3CH_3CO_2H + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$

(1)

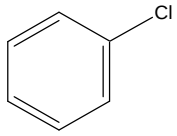
(b) i) Blood alcohol = 800mg/1000cm^3
Breath alcohol = 800/2300mg/1000cm^3 = 0.348mg/1000cm3 = 348µg/1000cm^3
(1)

ii) Max mass ethanol = 3 x 348 = 1.044mg/1000cm^3
∴ Max amount = 2.27 x 10^{-5}mol
Moles $K_2Cr_2O_7$ required = 2/3 x 2.27 x 10^{-5}
M_r ($K_2Cr_2O_7$) = 294
∴ Mass needed = 2/3 x 2.27 x 10^{-5} x 294 = 4.45mg
(3)

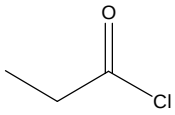
iii) Orange to green **(1)**

Total: 10

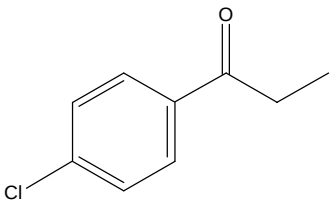
6. This question is about the synthesis of the new wonder-drug 'Rimonabant'



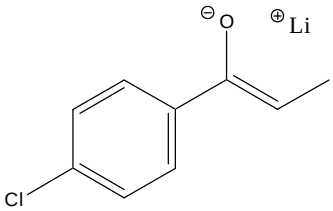
chlorobenzene



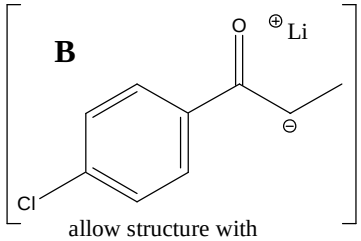
propanoyl chloride



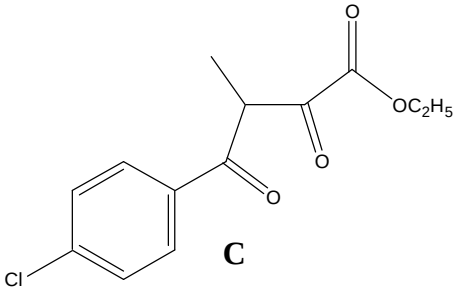
A



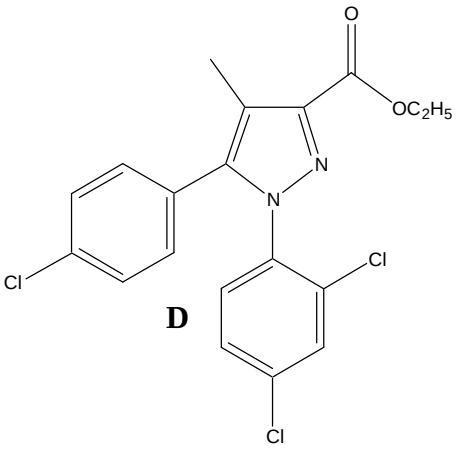
B



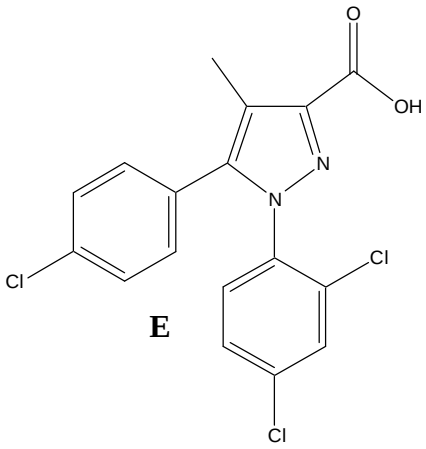
allow structure with
negative charge on carbon



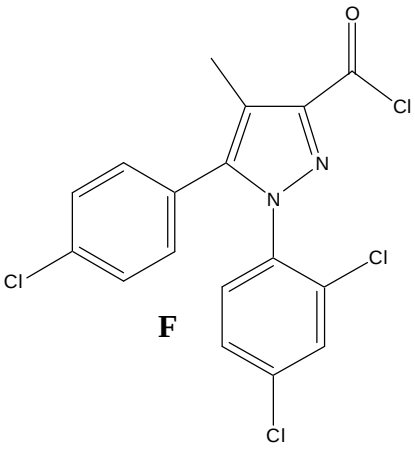
C



D



E



F

(1 mark for each structure
2 bonus marks if all correct)

Total: 8

Total for paper 64 (plus 2 possible bonus marks)