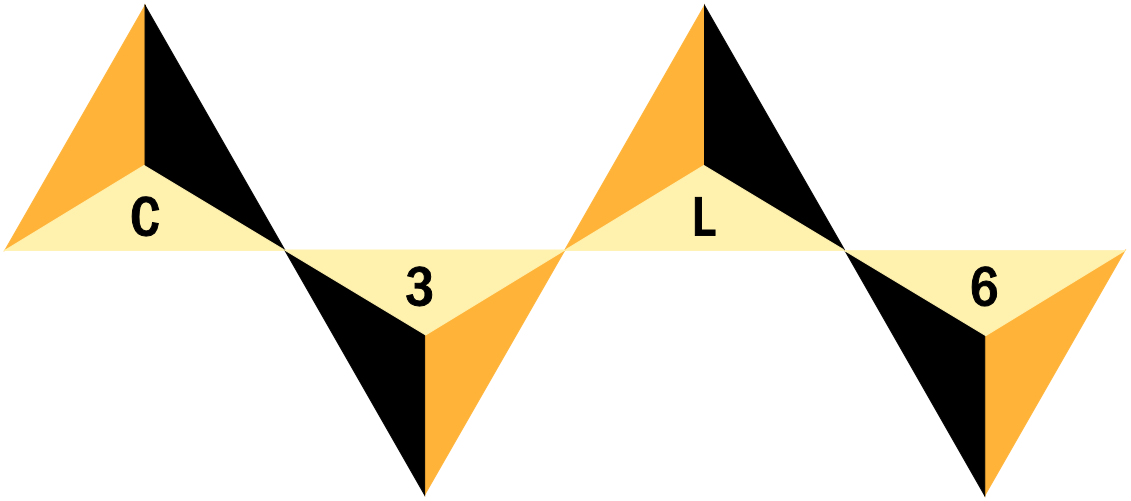


Cambridge Chemistry Challenge Lower 6th

June 2014

Some of the material in this booklet might be familiar to you, but other parts may be completely new. The questions are designed to be more challenging than those on typical AS papers, but you should still be able to attempt them. Use your scientific skills to work through the problems logically.

If you do become stuck on one part of a question, other parts might still be accessible, so do not give up. Good luck!

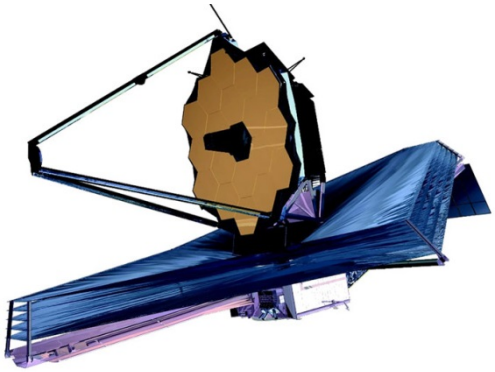
- The time allowed is 90 mins.
- Attempt all the questions.
- Write your answers in the answer booklet provided, giving only the essential steps in any calculations.
- Specify your answers to the appropriate number of significant figures and give the correct units.
- Please do not write in the right-hand margin.
- A periodic table and necessary constants are included on the next page.

1																	18
H 1 1.008	2											13	14	15	16	17	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01					**symbol** atomic number mean atomic mass						**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
Na 11 22.99	**Mg** 12 24.31	3	4	5	6	7	8	9	10	11	12	**Al** 13 26.98	**Si** 14 28.09	**P** 15 30.97	**S** 16 32.06	**Cl** 17 35.45	**Ar** 18 39.95
K 19 39.102	**Ca** 20 40.08	**Sc** 21 44.96	**Ti** 22 47.90	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.71	**Cu** 29 63.55	**Zn** 30 65.37	**Ga** 31 69.72	**Ge** 32 72.59	**As** 33 74.92	**Se** 34 78.96	**Br** 35 79.904	**Kr** 36 83.80
Rb 37 85.47	**Sr** 38 87.62	**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.94	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.4	**Ag** 47 107.87	**Cd** 48 112.40	**In** 49 114.82	**Sn** 50 118.69	**Sb** 51 121.75	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.30
Cs 55 132.91	**Ba** 56 137.34	**La*** 57 138.91	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.85	**Re** 75 186.2	**Os** 76 190.2	**Ir** 77 192.2	**Pt** 78 195.09	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.37	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
Fr 87	**Ra** 88	**Ac⁺** 89															

***Lanthanides**	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.4	**Eu** 63 151.96	**Gd** 64 157.25	**Tb** 65 158.93	**Dy** 66 162.50	**Ho** 67 164.93	**Er** 68 167.26	**Tm** 69 168.93	**Yb** 70 173.04	**Lu** 71 174.97
⁺Actinides	**Th** 90 232.01	**Pa** 91	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102	**Lr** 103

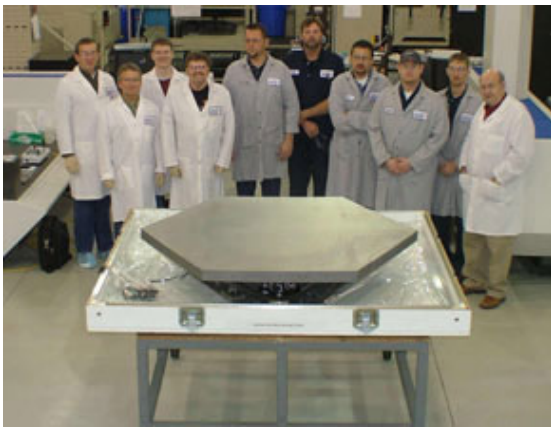
The Avogadro constant $N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$

1. This question is about beryllium in space



In December 2013, NASA took final delivery of the last of the 18 completed mirror segments that will make up the James Webb Space Telescope (JWST). Due for launch in 2018, this will be the most powerful telescope yet constructed.

Each hexagonal mirror segment is carved out of a hexagonal sheet of pure beryllium and is approximately 1.3 m in diameter and has a mass of 20.1 kg. In order to better reflect infrared light, the beryllium is coated with a thin layer of gold.



The beryllium used was extracted from the mineral *bertrandite*, mined in Utah, USA.

Preparation of metallic beryllium

Bertrandite contains the elements beryllium, silicon, hydrogen, and oxygen.

(a) (i) By considering their places in the periodic table or otherwise, give the most likely oxidation states of each of the four elements in bertrandite.

(ii) The empirical formula for bertrandite may be written $Be_4H_2O_xSi_2$.
Calculate the value of x.

The impure bertrandite is first treated with sulfuric acid which leaves the beryllium (and other metal ions) in solution as the sulfate. The first purification is by extracting the aqueous layer with hydrocarbon solvent containing di-(2-ethylhexyl)phosphoric acid, DEHPA. DEHPA is a diester of phosphoric(V) acid (H_3PO_4) and 2-ethylhexan-1-ol. The beryllium ions (and some other metal ions) interact with the DEHPA to form compounds which are soluble in the organic layer.

(b) (i) Draw the structure of 2-ethylhexan-1-ol.

(ii) Draw the structure for phosphoric(V) acid, H_3PO_4.

(iii) Suggest a structure for DEHPA.

On treatment with aqueous ammonium carbonate, most metal ions precipitate out, but the beryllium ions form ammonium beryllium carbonate, $(NH_4)_4Be(CO_3)_3$, which is highly soluble in water. After filtering, the solution is heated to 95 °C which causes a near quantitative precipitation of beryllium basic carbonate, $Be(OH)_2{\cdot}2BeCO_3$, and ammonia and carbon dioxide are evolved. On heating further at 165 °C, beryllium hydroxide is formed.

(c) (i) Give a balanced equation for the formation of beryllium basic carbonate from ammonium beryllium carbonate.

(ii) Give a balanced equation for the formation of beryllium hydroxide from wet beryllium basic carbonate.

After further purification, the beryllium hydroxide is eventually converted into beryllium fluoride, BeF_2. This is heated with magnesium metal to form elemental beryllium.

$$BeF_2(s) + Mg(s) \longrightarrow Be(s) + MgF_2(s)$$

(d) Given the standard enthalpy changes of formation at 298 K of BeF_2 and MgF_2 are –1010 and –1124 kJ mol^{-1} respectively, calculate the standard enthalpy change of reaction (at 298 K) for the formation of beryllium from BeF_2 according to the above equation.

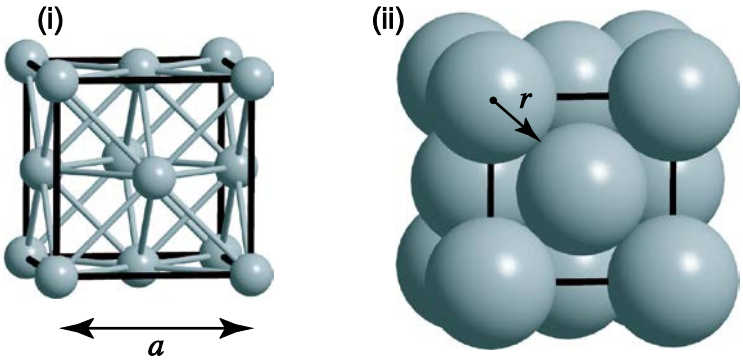
Properties of metallic beryllium

One of the reasons for choosing beryllium for the JWST mirrors was because of its high strength and low density (about 70% that of aluminium). Even though beryllium atoms are the fourth lightest of all the elements, perhaps surprisingly, calcium has the lowest density of the Group 2 elements. The density of an element depends on the mass of the atoms, the size of the atoms, and how well packed together they are.

(e) (i) Given the densities of beryllium and calcium are 1.85 and 1.55 g cm^{-3} respectively, calculate their molar volumes, i.e. the volume (in m^3) occupied by 1 mol.

(ii) Given that beryllium and calcium have exactly the same packing efficiencies (the fraction of the structure occupied by atoms), calculate the ratio of their atomic radii, r(Ca) / r(Be).

The unit cell, or repeating unit, for calcium is shown on the right. The structure of metallic calcium is generated by stacking these cubes together. It consists of a regular cube (shown with the dark lines with edge length a), with atoms placed so their centres are at the corners of the cube and in the centre of each face. In (i) the atoms in direct contact with each other are shown connected by the light coloured bonds. In (ii) the atoms are shown in direct contact with their nearest neighbours.

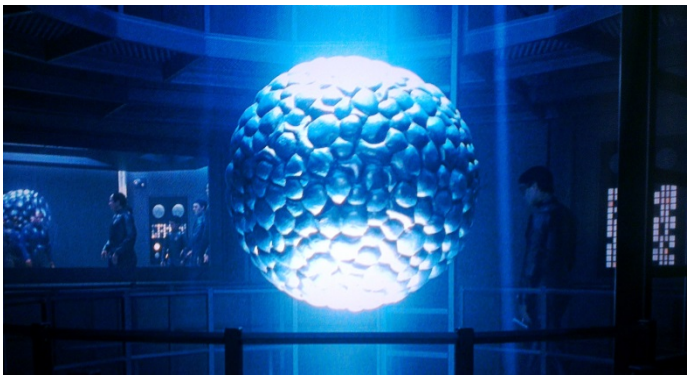


(f) (i) By adding up all the fractional parts of atoms contained within one unit cell, calculate the number of atoms contained in a cube of volume a^3.

(ii) Find an expression for the length, a, and hence volume of the cube in terms of the radius of the atom, r.

(iii) Given the density of calcium is 1.55 g cm^{-3}, calculate the atomic radius of calcium.

Beryllium in space travel



A beryllium sphere (shown right) supposedly powers the spaceship in the film *Galaxy Quest*. However, in *Star Trek*, another s-block element is used – lithium in the form of 'dilithium crystals'. Molecules of dilithium, Li_2, have been detected in the vapour above boiling lithium. The bond length in Li_2 is 267.3 pm and the bond dissociation enthalpy is 101.9 kJ mol^{-1}.

Unlike hydrogen which exists as stable H_2 molecules under standard conditions, lithium does not exist as Li_2 molecules but as lithium metal. This is because the formation of lithium metal from Li_2 molecules is strongly exothermic.

(g) Given the standard enthalpy change of formation of gaseous lithium atoms is 136 kJ mol^{-1}, calculate the enthalpy change for the reaction:

$$Li_2(g) \longrightarrow 2Li(s)$$

(h) Predict how the bond dissociation enthalpy and bond length will change if an electron is removed from $Li_2(g)$ molecule to form the $Li_2^+(g)$ ion. Tick the correct boxes in your answer booklet.

Diberyllium, Be_2, has also been detected in the gas phase but it has a very weak bond (bond dissociation enthalpy = 9.7 kJ mol^{-1}). The bond dissociation enthalpy and bond length change if one electron is removed from the molecule. In 2010 the first ionization energy of Be_2 molecules was measured to be 715.7 kJ mol^{-1}.

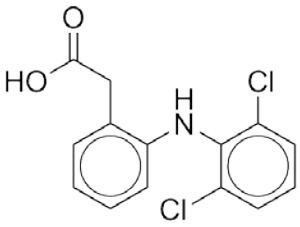
(i) **(i)** The first ionization energy of Be atoms is 899.5 kJ mol^{-1}. By constructing an appropriate thermodynamic cycle, calculate the bond dissociation enthalpy of $Be_2^+(g)$.

(ii) In light of your answer to part (i), predict how the bond length will change as an electron is removed from the $Be_2(g)$ molecule to form the $Be_2^+(g)$ ion.

2. This question is about dead vultures

Over the last twenty years, there has been a severe decline in the number of vultures living in the Indian subcontinent, with the numbers of some species falling by over 99%. As well as putting many species on the endangered list, this fall also meant the build-up of dead animal carcases, bringing with it an increase in disease and the number of rabid wild dogs.

In 2003, it was discovered that the anti-inflammatory drug Diclofenac (that was regularly administered to livestock) was fatal to the vultures that ate their carcases.



Diclofenac

$C_{14}H_{11}Cl_2NO_2$

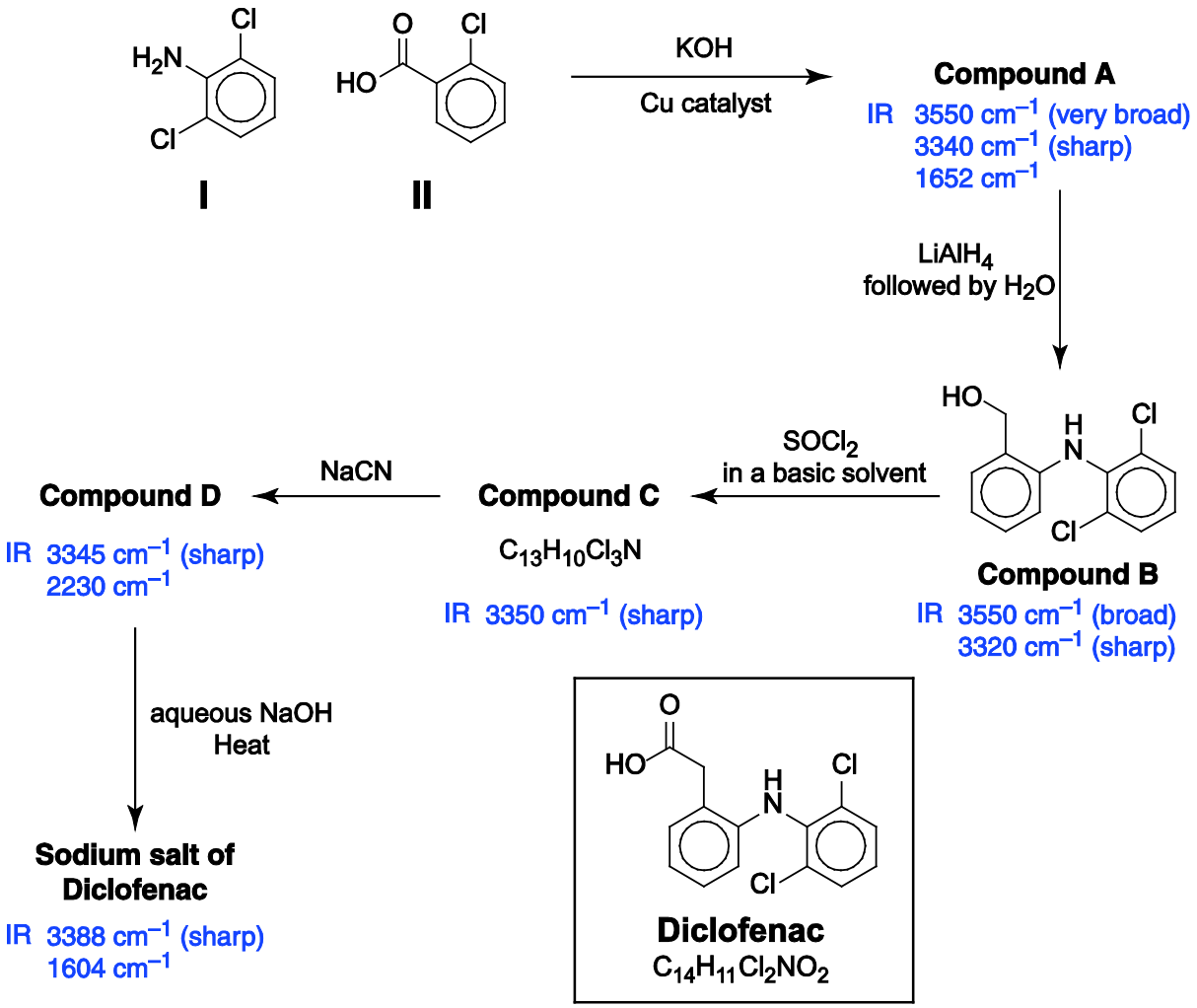
In this question skeletal formulae are used, where carbon atoms and hydrogens attached to carbon atoms are not drawn in explicitly. Benzene rings, C_6H_6 are represented as shown on the right.

Benzene

C_6H_6

Synthesis of Diclofenac

Diclofenac is synthesised from the two starting materials 2,6-dichloroaniline **(I)** and 2-chlorobenzoic acid **(II)**. The synthesis is shown over the page along with some of the key IR stretching frequencies of the compounds formed during the synthesis.



Compound A is formed from the reaction of one mole of KOH, one mole of **I**, and one mole of **II**. One mole of KCl and one mole of H_2O are formed as by-products of this reaction for every one mole of **Compound A** produced.

(a) **(i)** Give the molecular formulae of starting materials **I** and **II**.

(ii) By writing a balanced equation, deduce the formula of **Compound A**.

(iii) Suggest a structure for **Compound A**.

If **Compound A** is treated with $LiAlH_4$ followed by $HCl_{(aq)}$ instead of H_2O, **Compound B** is isolated as its hydrochloride salt. In this salt, the most basic atom in the molecule is protonated by the HCl.

(b) Suggest a structure for this hydrochloride salt including both the positive and negative ions, clearly indicating which atom is protonated.

$LiAlH_4$ consists of a Li^+ cation and an AlH_4^- anion. The AlH_4^- provides a source of H^-.

(c) **(i)** How would you classify the reagent AlH_4^-? (Circle your choice in the answer booklet.)

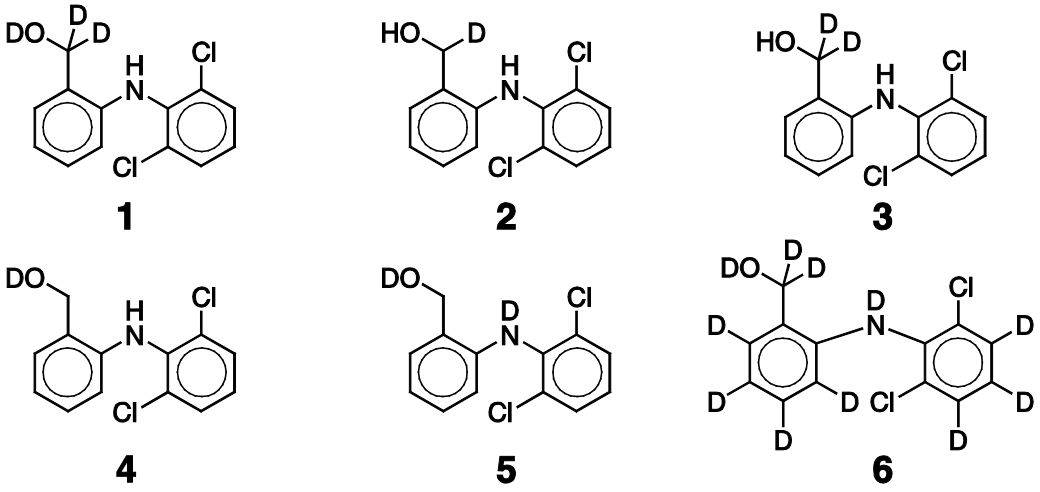
Nucleophile Electrophile Radical Catalyst

(ii) How would you classify the reaction of **Compound A** to **Compound B**? (Circle your choice in the answer booklet.)

Hydrolysis Condensation Oxidation Reduction Isomerisation

It is possible to incorporate deuterium atoms into **Compound B** by using deuterated reagents in the reaction of **Compound A** to **Compound B**. A deuterated reagent has some or all of its hydrogen atoms (^{1}H) replaced by deuterium atoms (^{2}H or D).

(d) Suggest which of the structures below (**1**-**6**) would be the product of the reaction if the following reagents were used instead.



(i) **Compound A** $\xrightarrow[\text{followed by } D_2O]{LiAlH_4}$ **Compound B^1**

(ii) **Compound A** $\xrightarrow[\text{followed by } H_2O]{LiAlD_4}$ **Compound B^2**

(e) **(i)** NaCN consists of an Na^+ cation and a $^-C{\equiv}N$ anion. How would you classify the reagent $^-C{\equiv}N$? (Circle your choice in the answer booklet.)

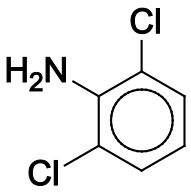
Nucleophile Electrophile Radical Catalyst

(ii) Suggest structures for intermediate **Compounds C** and **D**.

(f) Assign each of the following sets of IR strectching frequencies to a particular bond stretch.

(i) 3550 cm^{-1} (broad)
(ii) 3320-3390 cm^{-1} (sharp)
(iii) 2230 cm^{-1}
(iv) 1652 cm^{-1}
(v) 1604 cm^{-1}

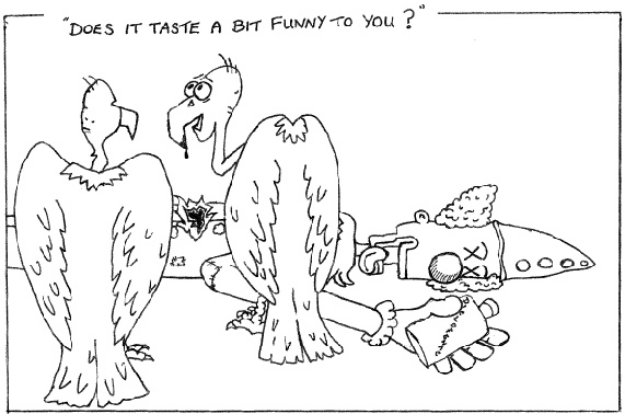
When the drug Diclofenac was being developed, alternative starting materials to 2,6-dichloroaniline (**I**) were investigated where there were substituents on other places on the benzene ring. It was discovered that only benzene rings that had adjacent substituents both sides of the nitrogen were active.



2,6-dichloroaniline (I)

(g) Draw all the possible isomers of dichloroaniline, where both chlorine atoms are attached to the benzene ring.

Detecting Diclofenac in vultures



The presence of Diclofenac in the dead vultures was detected using mass spectrometry. The mass spectrometer that was used for the analysis produced negatively charged ions, unlike the more familiar instruments that produce positively charged ions. The molecular formula of Diclofenac is $C_{14}H_{11}Cl_2NO_2$.

(h) In the mass spectrum produced by this instrument, the most abundant ion had a formula of $[C_{14}H_{10}Cl_2NO_2]^-$. Suggest a structure for this anion.

This anion gives a number of peaks in the mass spectrum due to the different isotopes of the elements that are present.

Isotopic Abundances (other elements assume lightest isotope only)

Carbon – ^{12}C 98.9%, ^{13}C 1.1%	Chlorine – ^{35}Cl 75.8%, ^{37}Cl 24.2%

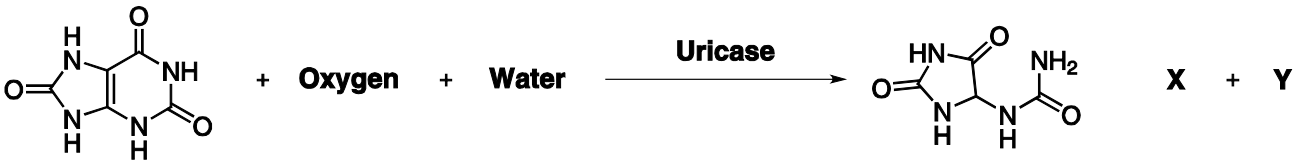
The most abundant peak from this anion is at mass to charge (m/z) ratio of 294 and is due to the lightest isotope of each element being present, i.e. $[(^{12}C)_{14}(^{1}H)_{10}(^{35}Cl)_2(^{14}N)(^{16}O)_2]^-$

(i) What is the height of this peak as a percentage of the total of the height of all the peaks from the $[C_{14}H_{10}Cl_2NO_2]^-$ anion?

(j) **(i)** Give all possible isotopic formulae of this anion that would give a peak at an m/z of 295.

(ii) What is the height of this peak at 295 as a percentage of the total of the height of all the peaks from this anion?

Diclofenac is lethal to vultures as it stops their kidneys functioning properly, leading to a build-up of toxic amounts of uric acid. In order to determine the amount of uric acid in the vultures, the uric acid was first converted into allantoin with the enzyme uricase in the reaction below.



Uric Acid **Allantoin**

Two other products are formed, liquid **X** and gas **Y**. Both **X** and **Y** contain two oxygen atoms.

(k) **(i)** Give the molecular formulae for uric acid and allantoin.

(ii) Suggest an identity for liquid **X** and gas **Y**.

(iii) Write a balanced equation for the reaction.

The amount of liquid **X** can be determined quantitatively by reacting it with a compound called 4-AAP to form a red compound that strongly absorbs light. 1.0 g of vulture tissue (of density 1.0 g cm^{-3}) was liquefied and diluted by a factor of 20. After reaction with uricase and addition of 4-AAP, the sample was placed in a colorimeter where it was found that it had a concentration of 230 μmol dm^{-3} of **X**.

(l) Calculate the amount of uric acid in the vulture in mg / kg of tissue.

Acknowledgements

We would like to thank those who support C3L6:

Saudi Aramco

University of Cambridge International Examinations

OCR

The Royal Society of Chemistry

University of Cambridge Department of Chemistry

St Catharine's College, Cambridge

Question 1

Pictures from NASA JWST website, and from the film *Galaxy Quest*

There is much information freely available from the NASA website concerning the James Webb Space Telescope:

http://jwst.nasa.gov

A great video showing the extraction of beryllium from bertrandite:

http://webbtelescope.org/webb_telescope/behind_the_webb/episodes/9

Question 2 was based on the paper:

Nature, **427**, (12 February 2004) 630-633
"*Diclofenac residues as the cause of vulture population decline in Pakistan*"
J. Lindsay Oaks *et al*.

A number of recent articles may also be found online.

Thanks to Adam Loveday for the cartoon.