HL Paper 2

Urea, $(H_2N)_2CO$, is excreted by mammals and can be used as a fertilizer.

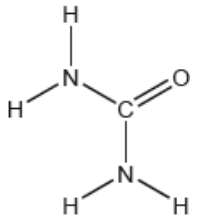
Urea can also be made by the direct combination of ammonia and carbon dioxide gases.

$$2NH_3(g) + CO_2(g) \rightleftharpoons (H_2N)_2CO(g) + H_2O(g) \quad \Delta H < 0$$

a.i. Calculate the percentage by mass of nitrogen in urea to two decimal places using section 6 of the data booklet. [2]

a.ii. Suggest how the percentage of nitrogen affects the cost of transport of fertilizers giving a reason. [1]

b. The structural formula of urea is shown. [3]



Predict the electron domain and molecular geometries at the nitrogen and carbon atoms, applying the VSEPR theory.

	Electron domain geometry	Molecular geometry
Nitrogen	. . . . .	. . . . .
Carbon	. . . . .	trigonal planar

c. Urea can be made by reacting potassium cyanate, KNCO, with ammonium chloride, NH_4Cl. [2]

$$KNCO(aq) + NH_4Cl(aq) \rightarrow (H_2N)_2CO(aq) + KCl(aq)$$

Determine the maximum mass of urea that could be formed from 50.0 cm^3 of 0.100 mol dm^{-3} potassium cyanate solution.

d.i. State the equilibrium constant expression, K_c. [1]

d.ii. Predict, with a reason, the effect on the equilibrium constant, K_c, when the temperature is increased. [1]

d.iii. Determine an approximate order of magnitude for K_c, using sections 1 and 2 of the data booklet. Assume $\Delta G^{\ominus}$ for the forward reaction is approximately +50 kJ at 298 K. [2]

e.i. Suggest one reason why urea is a solid and ammonia a gas at room temperature. [1]

e.ii. Sketch two different hydrogen bonding interactions between ammonia and water. [2]

f. The combustion of urea produces water, carbon dioxide and nitrogen. [2]

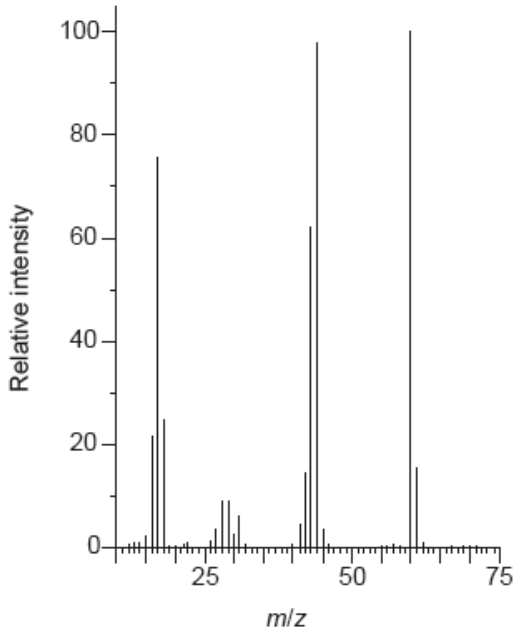
Formulate a balanced equation for the reaction.

g. Calculate the maximum volume of CO_2, in cm^3, produced at STP by the combustion of 0.600 g of urea, using sections 2 and 6 of the data booklet. [1]

h. Describe the bond formation when urea acts as a ligand in a transition metal complex ion. [2]

i. The C–N bonds in urea are shorter than might be expected for a single C–N bond. Suggest, in terms of electrons, how this could occur. [1]

j. The mass spectrum of urea is shown below. [2]



[Source: http://sdbs.db.aist.go.jp]

Identify the species responsible for the peaks at m/z = 60 and 44.

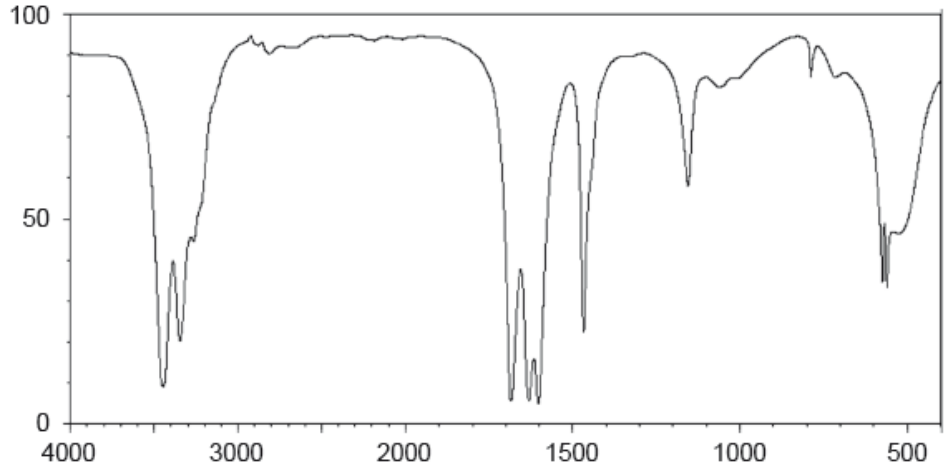
60:

. . . . . .

44:

. . . . . .

k. The IR spectrum of urea is shown below. [2]



[Source: sdbs.db.aist.go.jp]

Identify the bonds causing the absorptions at 3450 cm^{-1} and 1700 cm^{-1} using section 26 of the data booklet.

3450 cm^{-1}:

. . . . . .

1700 cm^{-1}:

. . . . . .

I.i. Predict the number of signals in the ^1H NMR spectrum of urea. [1]

I.ii. Predict the splitting pattern of the ^1H NMR spectrum of urea. [1]

I.iii. Outline why TMS (tetramethylsilane) may be added to the sample to carry out ^1H NMR spectroscopy and why it is particularly suited to this role. [2]

This question is about carbon and chlorine compounds.

a. Ethane, C_2H_6, reacts with chlorine in sunlight. State the type of this reaction and the name of the mechanism by which it occurs. [1]

Type of reaction:

. . . . . .

Mechanism:

. . . . . .

b.i. Formulate equations for the two propagation steps and one termination step in the formation of chloroethane from ethane. [3]

Two propagation steps:

. . . . . .

. . . . . .

. . . . . .

. . . . . .

One termination step:

. . . . . .

. . . . . .

b.ii. Deduce the splitting patterns in the ^{1}H NMR spectrum of C_2H_5Cl. [1]

b.iii. Explain why tetramethylsilane (TMS) is often used as a reference standard in ^{1}H NMR. [2]

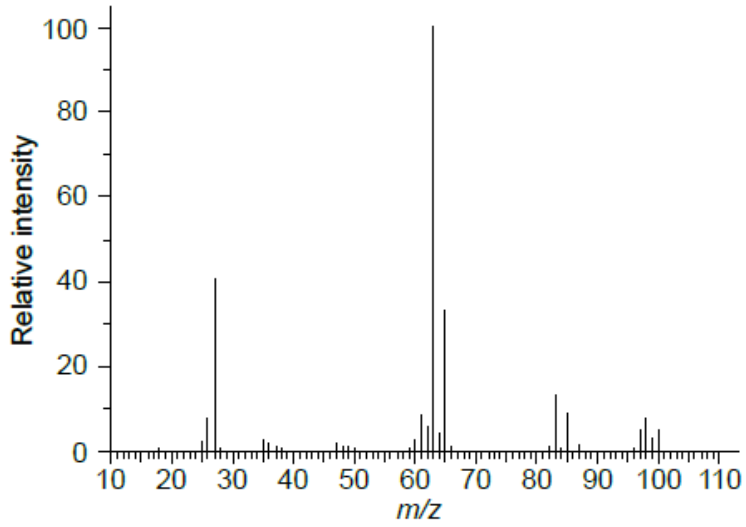
c.i. One possible product, **X**, of the reaction of ethane with chlorine has the following composition by mass: [2]

carbon: 24.27%, hydrogen: 4.08%, chlorine: 71.65%

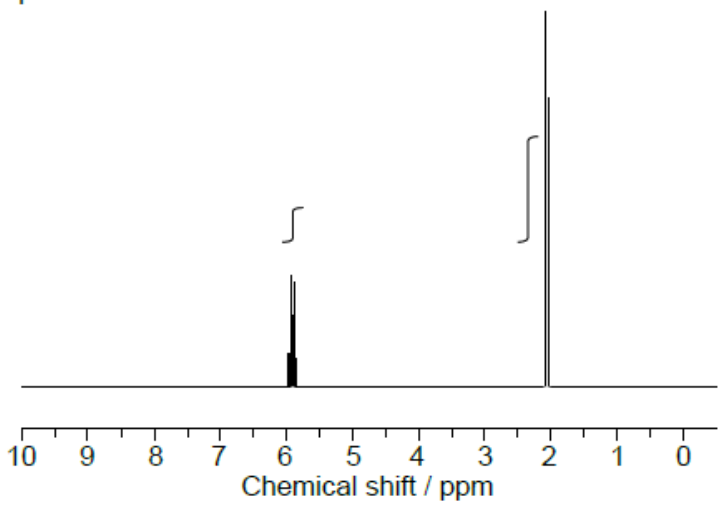
Determine the empirical formula of the product.

c.ii. The mass and ^{1}H NMR spectra of product **X** are shown below. Deduce, giving your reasons, its structural formula and hence the name of the compound. [3]

Mass spectrum:



^{1}H NMR spectrum:



[Source: http://sdbs.db.aist.go.jp]

c.iii When the product **X** is reacted with NaOH in a hot alcoholic solution, C_2H_3Cl is formed. State the role of the reactant NaOH other than as a nucleophile. [1]

d. Chloroethene, C_2H_3Cl, can undergo polymerization. Draw a section of the polymer with three repeating units. [1]

Ethane-1,2-diol, $HOCH_2CH_2OH$, has a wide variety of uses including the removal of ice from aircraft and heat transfer in a solar cell.

b. (i) Calculate ΔH^θ, in kJ, for this similar reaction below using ΔH_f^θ data from section 12 of the data booklet. ΔH_f^θ of $HOCH_2CH_2OH(l)$ is –454.8kJmol^{-1}. [6]

$$2CO\ (g) + 3H_2\ (g) \rightleftharpoons HOCH_2CH_2OH\ (l)$$

(ii) Deduce why the answers to (a)(iii) and (b)(i) differ.

(iii) ΔS^θ for the reaction in (b)(i) is –620.1JK^{-1}. Comment on the decrease in entropy.

(iv) Calculate the value of ΔG^θ, in kJ, for this reaction at 298 K using your answer to (b)(i). (If you did not obtain an answer to (b)(i), use –244.0 kJ, but this is not the correct value.)

(v) Comment on the statement that the reaction becomes less spontaneous as temperature is increased.

f. Predict the ^{1}HNMR data for ethanedioic acid and ethane-1,2-diol by completing the table. [2]

	Number of signals	Splitting pattern
Ethanedioic acid:	.....	.....
Ethane-1,2-diol:	.....	Not required

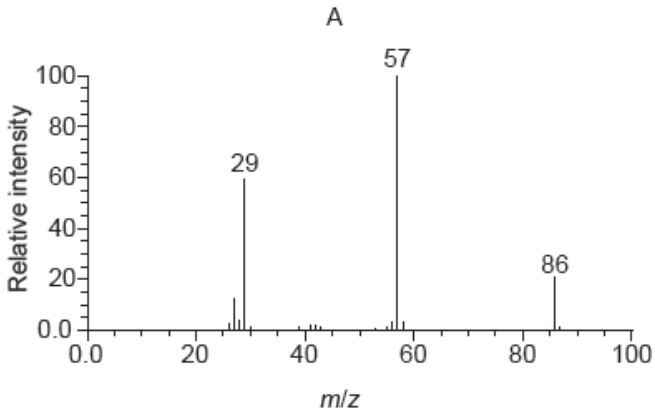
Organic compounds often have isomers.

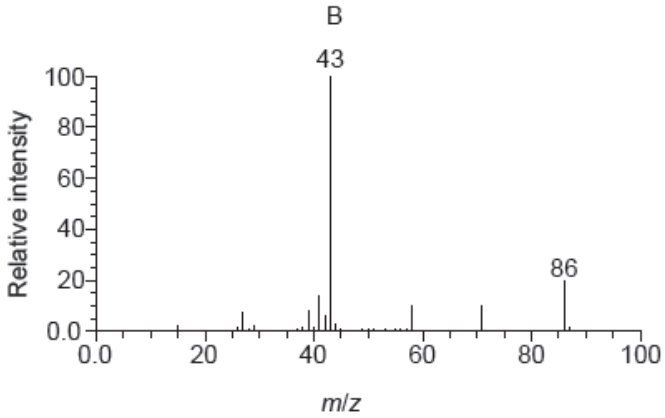
A straight chain molecule of formula $C_5H_{10}O$ contains a carbonyl group. The compound cannot be oxidized by acidified potassium dichromate(VI) solution.

A tertiary halogenoalkane with three different alkyl groups, $(R_1R_2R_3)C–X$, undergoes a S_N1 reaction and forms two isomers.

a.i. Deduce the structural formulas of the two possible isomers. [2]

a.ii. Mass spectra **A** and **B** of the two isomers are given. [2]





[Source: NIST Mass Spec Data Center, S.E. Stein, director, "Mass Spectra" in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303, (retrieved May 31, 2018).]

Explain which spectrum is produced by each compound using section 28 of the data booklet.

A:

. . . . . .

. . . . . .

B:

. . . . . .

. . . . . .

b.i. State the type of bond fission that takes place in a S_N1 reaction. [1]

b.ii. State the type of solvent most suitable for the reaction. [1]

b.iii. Draw the structure of the intermediate formed stating its shape. [2]

Shape:

. . . . . .

b.iv. Suggest, giving a reason, the percentage of each isomer from the S_N1 reaction. [2]

c. Nitrobenzene, $C_6H_5NO_2$, can be converted to phenylamine via a two-stage reaction. [2]

In the first stage, nitrobenzene is reduced with tin in an acidic solution to form an intermediate ion and tin(II) ions. In the second stage, the intermediate ion is converted to phenylamine in the presence of hydroxide ions.

Formulate the equation for each stage of the reaction.

Stage one:

. . . . . .

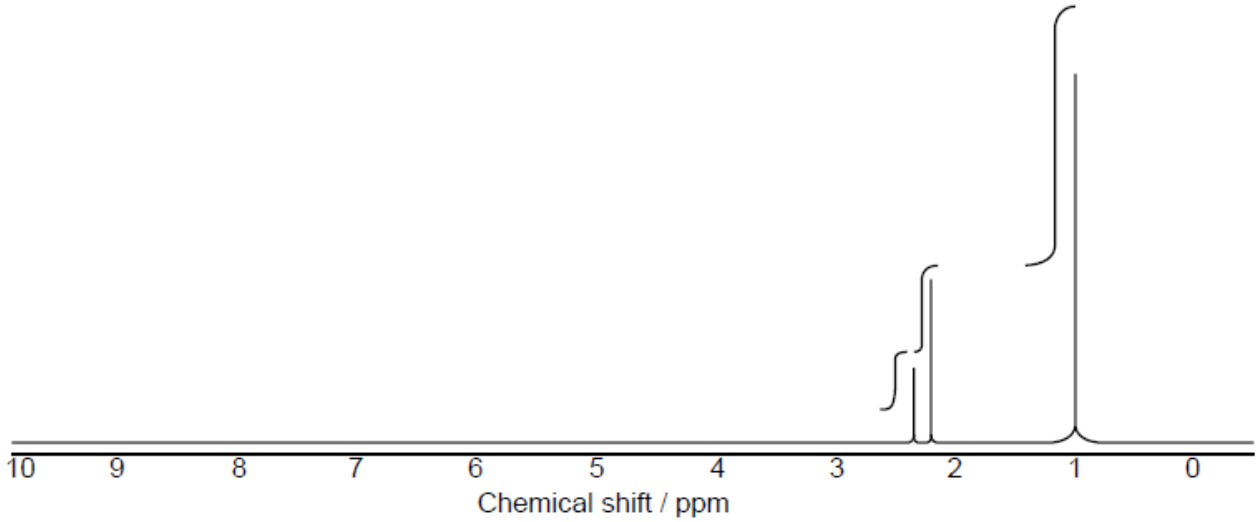
. . . . . .

Stage two:

. . . . . .

. . . . . .

A compound with a molecular formula $C_7H_{14}O$ produced the following high resolution ^1H NMR spectrum.



a.i. Deduce what information can be obtained from the ^1H NMR spectrum. [3]

Number of hydrogen environments:

. . . . . .

Ratio of hydrogen environments:

. . . . . .

Splitting patterns:

. . . . . .

a.ii. Identify the functional group that shows stretching at 1710 cm^{-1} in the infrared spectrum of this compound using section 26 of the data booklet and the ^1H NMR. [1]

a.iii. Suggest the structural formula of this compound. [2]

b.i. Bromine was added to hexane, hex-1-ene and benzene. Identify the compound(s) which will react with bromine in a well-lit laboratory. [1]

b.ii. Deduce the structural formula of the main organic product when hex-1-ene reacts with hydrogen bromide. [1]

c.i. State the reagents and the name of the mechanism for the nitration of benzene. [2]

Reagents:

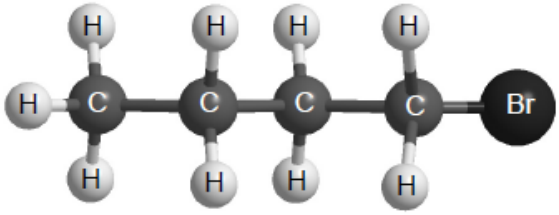
. . . . . .

Name of mechanism:

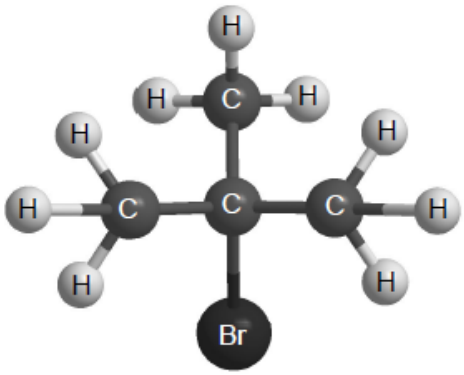
. . . . . .

c.ii.Outline, in terms of the bonding present, why the reaction conditions of halogenation are different for alkanes and benzene. [1]

d. Below are two isomers, A and B, with the molecular formula C_4H_9Br. [3]



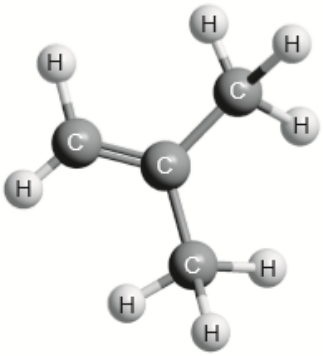
A



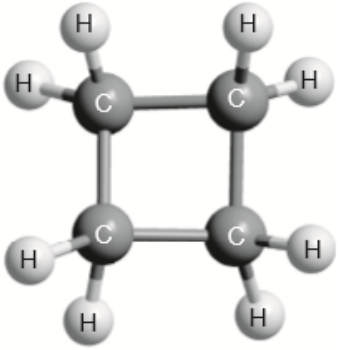
B

Explain the mechanism of the nucleophilic substitution reaction with NaOH(aq) for the isomer that reacts almost exclusively by an S_N2 mechanism using curly arrows to represent the movement of electron pairs.

Compound **A** and compound **B** are hydrocarbons.



A



B

a. (i) State the term that is used to describe molecules that are related to each other in the same way as compound **A** and compound **B**. [3]

(ii) Suggest a chemical test to distinguish between compound **A** and compound **B**, giving the observation you would expect for each.

Test:

Observation with **A**:

Observation with **B**:

b. Outline how you could use the IR spectra of compounds **A** and **B** and section 26 of the data booklet to identify them. [1]

c. Two signals occur in the ^1H NMR spectrum of compound **A**. Deduce their expected chemical shift and their splitting pattern, using section 27 of the data booklet. [2]

Signal	1	2
Chemical shift / ppm	. . . . .	. . . . .
Splitting pattern	. . . . .	. . . . .