IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2013, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

CHEMISTRY FOUNDATION PAPER TWO

Friday 11th January 2013, 09:30-11:30

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

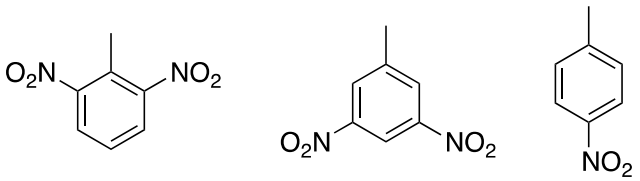
1IS1 (1) – Introduction to Spectroscopy and Characterisation

N.B. This question is worth 25 marks

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

Nitrotoluene compounds are known precursor compounds to forming trinitrotoluene. The structure of three of this class of compound are shown below.



X Y Z

i) Sketch the ^{1}H NMR spectrum of 2,6-dinitrotoluene (X), 3,5-dinitrotoluene (Y) and 4-nitrotoluene (Z), paying attention to the chemical shifts, integrals and multiplicities of the resonances.

[You may assume coupling only occurs through 3 bonds or fewer; that for ^{1}H, I = ½, is 100% abundant; ignore coupling to other nuclei]

(10 marks)

These compounds may also be analysed using mass spectrometry. Electron ionisation spectrometry (EI-MS) will show a full fragmentation pattern, while electrospray ionisation spectrometry (ESI-MS) will tend to only show the molecular ion peak.

ii) Explain the difference between EI-MS and ESI-MS techniques, and account for the difference in mass spectrum described above.

(5 marks)

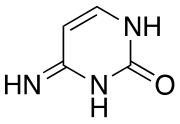
QUESTION CONTINUED OVERLEAF

b) Answer **ALL** parts of this question.

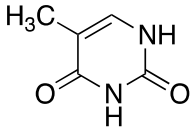
Infra-red spectra are run on two samples, A and B; the major peaks of these spectra are listed below.

Compound A	Compound B
3205 cm^{-1}	3383 cm^{-1}
3191 cm^{-1}	3173 cm^{-1}
1743 cm^{-1}	2797 cm^{-1}
1680 cm^{-1}	1663 cm^{-1}

It is known that A and B are either **cytosine** or **thymine**; these structures are shown below:



Cytosine



Thymine

i) From the data and structures provided, assign the frequencies to bond vibrations, and identify compounds A and B.

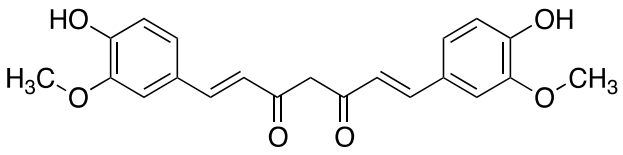
(6 marks)

ii) From your knowledge of spectroscopic techniques, identify **one** other technique which could be used to identify A and B. Explain what you would expect to see from the spectra recorded, using sketches if necessary.

(4 marks)

QUESTION CONTINUED OVERLEAF

c) Answer **ALL** parts of this question.



Curcumin

Curcumin (shown above) shows a strong colour change in the presence of cyanide ions; the wavelength of maximum absorbance changes from 507 nm to 649 nm in the presence of CN^-.

i) What colour is observed in A) the presence and B) the absence of CN^-?
ii) Calculate the energy of each transition, expressing your answer in wave numbers.
iii) Why are UV/Vis peaks broader than IR peaks?

Give reasons for your answers (6 marks)

iv) An IR spectrum of curcumin is recorded, and the following peak frequencies are observed: 3379 cm^{-1}, 1628 cm^{-1}, 1593 cm^{-1}, 1512 cm^{-1}, 1285 cm^{-1}. Using the structure of curcumin shown, assign the vibration frequencies.

(4 marks)

1IS1 (2) – Introduction to Spectroscopy & Characterisation

N.B. This question is worth 25 marks

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Answer **ALL** parts of this question.

i) Absorption due to the vibration of the Co-H bond in $Co(CO)_4H$ is seen in the IR at a wavelength of 5.17 μm. Calculate

1) the frequency of light

(1 mark)

2) the energy absorbed by the molecule in the spectroscopic transition.

(1 mark)

ii) In the far infrared spectrum of $^{39}K^{35}Cl$ there is an intense line at 378 cm^{-1}.
Calculate the force constant of the KCl bond.

(3 marks)

iii) The rotational constant of $^{127}I^{35}Cl$ is 0.1142 cm^{-1}. Calculate the ICl bond length.

(3 marks)

iv) State the selection rule for rotational spectra. Which of the following gas molecules satisfy it and have pure microwave absorption spectra:
H_2, HF, CH_4, CH_3CH_3, CH_3Cl, CH_2Cl_2, O_2

(3 marks)

v) How many normal modes of vibration are there for each molecule

1) HCN
2) C_2H_4
3) C_6H_6 ? Justify your answer in each case.

(3 marks)

b) Answer **ALL** parts of this question.

i) Write the expression of the energy levels of rotation within the rigid rotor approximation.

(1 mark)

QUESTION CONTINUED OVERLEAF

ii) Suppose the selection rule for rotational transitions were not $\Delta J = \pm 1$ but $\Delta J = \pm 3$.
Derive the separation between neighbouring rotational peaks in this case, assuming the rigid rotor approximation.

(4 marks)

iii) The spacing of the lines in the microwave spectrum of $^{27}Al^{1}H$ is constant at 12.604 cm^{-1}.
Calculate the moment of inertia and bond length of the molecule.

(4 marks)

iv) State the limitations of the rigid rotor model.

(2 marks)

c) Answer **ALL** parts of this question.

i) The force constant for HBr is 411.5 Nm^{-1}. Calculate the ratio of population of the first excited vibrational state relative to the ground state of HBr at 300 K.

(6 marks)

ii) Comment on your result.

(1 mark)

iii) Which of the following molecules show infrared absorption spectra? Justify your answer.

1) H_2
2) HCl
3) CO_2
4) CH_4

(4 marks)

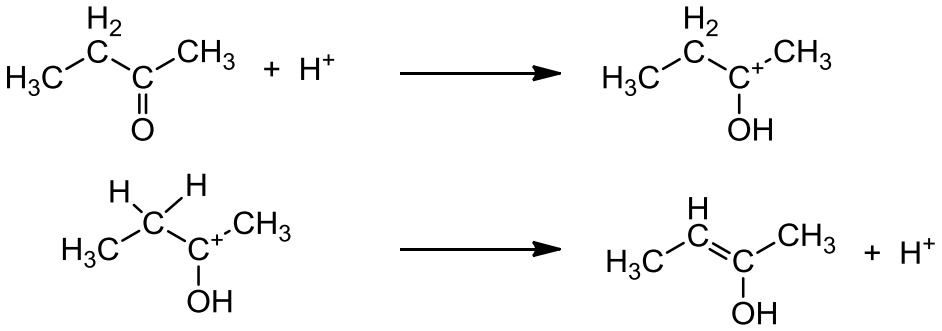
1F1 – Reactivity and Characterisation

NB. 'Half a question' (out of 12.5 marks)

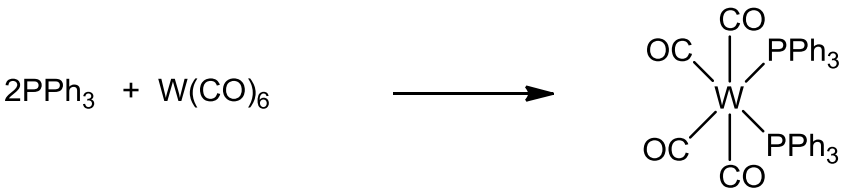
Give the reaction type for **THREE** of the following reactions. For the reactions of metal containing compounds give the oxidation state for **ALL** metal atoms. For other reactions draw appropriate arrows to indicate the direction of electron flow.

a) $Cl^- + H_3C\text{-}OCF_3 \longrightarrow CH_3Cl + CF_3O^-$

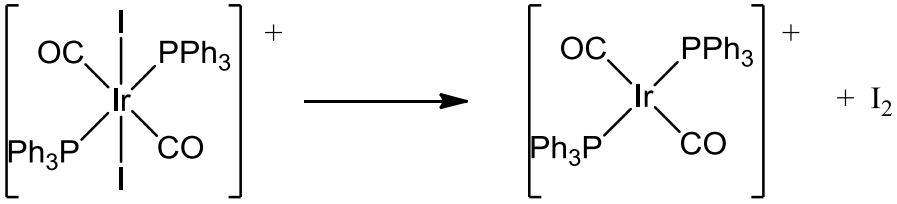
b)



c)



d)



(4 marks each plus 0.5 bonus mark)