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

ADVANCED CHEMISTRY THEORY IIIA

Paper 2

Wednesday 09th January 2013, 09:30-11:45

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

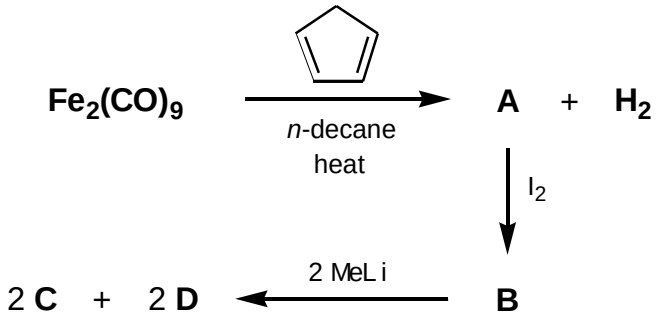
USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.

3.I3 – Advanced Transition Metal Chemistry

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

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

Compound **A** has empirical formula $C_{14}H_{10}Fe_2O_4$ and displays two absorptions in the infrared spectrum at 1960 cm^{-1} and 1765 cm^{-1}. Compound **B** has the empirical formula $C_7H_5FeIO_2$ and gives rise to a singlet in the ^1H NMR spectrum and two absorptions at 2055 cm^{-1} and 1950 cm^{-1} in the infrared spectrum. Compound **C** shows two singlets in the ^1H NMR spectrum in the ratio 5:3, while **D** is a colourless, water soluble solid.



i) Draw structures for the organometallic compounds **A** – **C** and give the identity of compound **D**. State the oxidation states of all iron compounds including diiron nonacarbonyl.

(5 marks)

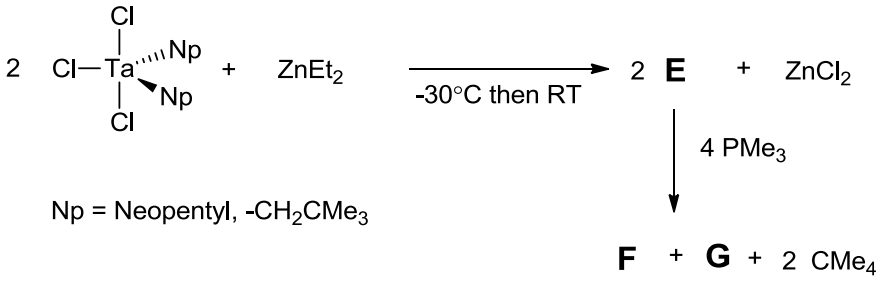
ii) Explain the infrared and NMR data provided.

(3 marks)

QUESTION CONTINUED OVERLEAF

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

Compound **E** slowly decomposes at room temperature, but is stable at -30°C. Addition of PMe_3 to compound **E** results in the formation of an equimolar mixture of compounds **F** and **G,** as well as 2,2-dimethylpropane. Compounds **F** and **G** each contain two PMe_3 ligands and result from two competitive elimination processes. The ^{31}P NMR spectra of both compounds **F** and **G** show only one signal each.



i) Propose a structure for organometallic compound **E**. Explain the choice of $ZnEt_2$ and reaction conditions for the formation of compound **E**.

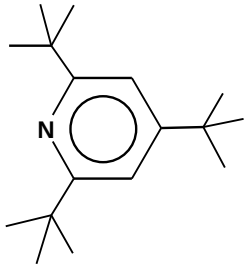
(1 mark)

ii) Draw the structures of compounds **F** and **G**. Identify the reactions that generate each product and describe the factors that favour each of these transformations.

(6 marks)

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

The ^1H NMR spectrum of $[Ti(\eta^6\text{-tbpy})_2]$ shows three resonances of equal integration (1:1:1) attributable to *tertiary*-butyl groups. However, the ^1H NMR spectrum of the analogous zirconium compound, $[Zr(\eta^6\text{-tbpy})_2]$, shows only two resonances which can be assigned to *tertiary*-butyl groups, with an integration ratio of 2:1. The tbpy ligand is shown below.



QUESTION CONTINUED OVERELAF

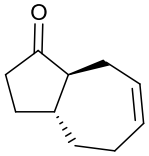
i) Draw the structures of the titanium and zirconium compounds and explain how they are consistent with the observed NMR spectra.

(8 marks)

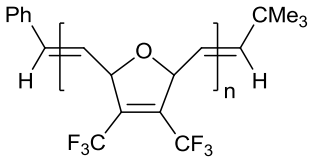
ii) Explain why coordination only through the nitrogen of the tbpy ligand does not occur.

(2 marks)

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



H



I

Complexes of general formula [M=CHR] can be used to prepare compounds **H** and **I**.

i) Draw the structure of the organic precursors for the synthesis of both compounds **H** and **I**.

(2 marks)

ii) Describe the general mechanism for the formation of **I**.

(2 marks)

iii) Propose two different plausible combinations of metal complex [M=CHR] and termination reagent for the preparation of **I**.

(4 marks)

iv) What type of metal compound is obtained at the end of the polymerization?

(2 marks)

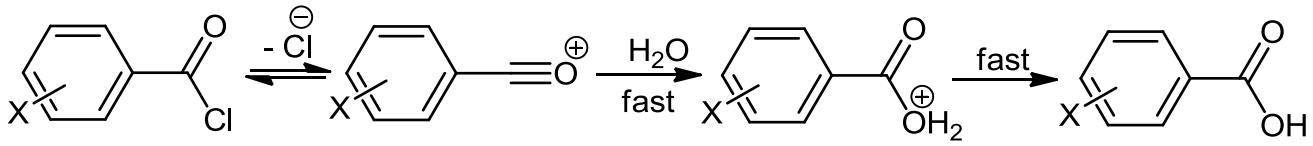
3.O4 – Introduction to Physical Organic Chemistry

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

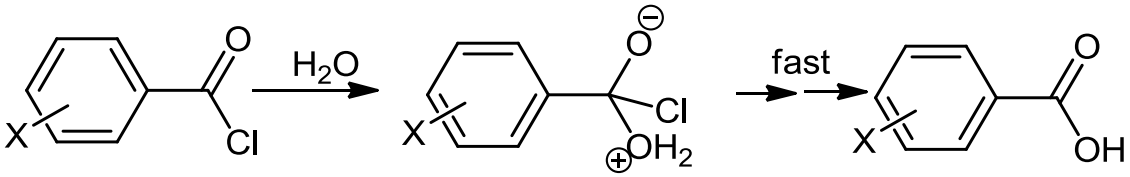
a) Answer **ALL** parts of this question.

i) The hydrolysis of a series of substituted aryl acid chlorides can occur by either Mechanism 1 or Mechanism 2, shown below, depending on the choice of substituents on the aryl ring.

Mechanism 1



Mechanism 2



A. Sketch the expected Hammett plot for a series of substituents with both +ve and –ve substituent constants.

(2 marks)

B. Explain how the mechanism change affects the shape of the plot.

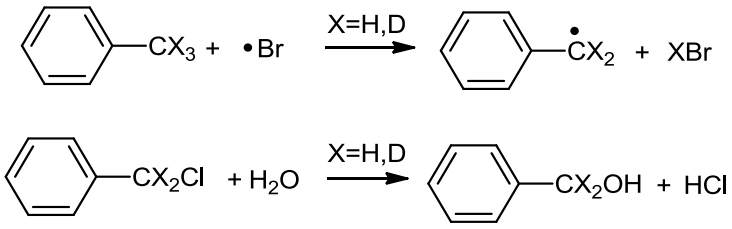
(4 marks)

C. Predict whether the magnitudes of the reaction constant ρ for both parts of the plot are greater or less than unity.

(2 marks)

QUESTION CONTINUED OVERLEAF

ii) The following two reactions exhibit primary, secondary or inverse kinetic isotope effects.



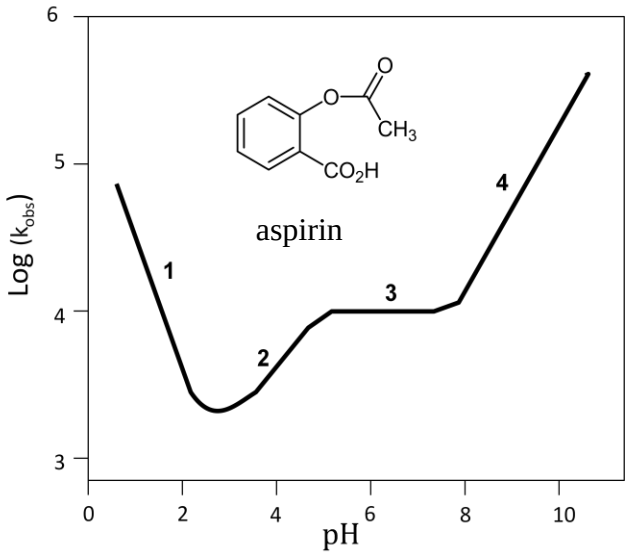
A. For both reactions, state which kinetic isotope effect will occur.

(2 marks)

B. Predict an approximate k_H/k_D value for both reactions.

(2 marks)

iii) The rate of hydrolysis of aspirin was studied at a range of pHs and the rate profile is shown below. The profile is divided into four sections 1-4.



A. Choose any two sections and identify the mechanism of hydrolysis.

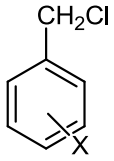
(2 marks)

B. For both of your chosen sections, draw the mechanisms.

(4 marks)

QUESTION CONTINUED OVERLEAF

iv) The rate of hydrolysis of the substituted aryl chloride below was studied with a range of substituents and the Hammett plot exhibited a concave up deviation to linearity.



A. What is the reason for the nonlinearity?

(1 mark)

B. How can the entropy of activation measurements of the reactions be used to differentiate between the two sides of the Hammett plot?

(2 marks)

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

The following two reactions have either a reaction constant of 2.45 or 0.75.
Ionization of substituted benzenethiols.
Ionization of substituted benzenephosphonic acids.

i) Match the appropriate reactions with the given ρ values.

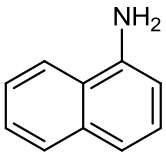
(1 mark)

ii) Explain your reasoning.

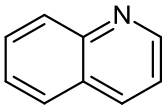
(3 marks)

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

The pK_a values of the conjugate acids of 1-naphthylamine and quinoline (shown below) are 3.85 and 4.88 respectively.



1-naphthylamine



quinoline

i) Explain the difference in pK_a.

(2 marks)

ii) The pK_a value of the conjugate acid of phenylamine is 4.6. Write both balanced equations for the reaction of phenylamine with the conjugate acid of the two bases above, indicating which side of the reaction the equilibrium is favoured.

(2 marks)

3.P9 – Photochemistry

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

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

i) With the aid of a diagram define the terms: fluorescence, phosphorescence, internal conversion, intersystem crossing, singlet and triplet states. Briefly discuss the factors that influence the rate of internal conversion in a molecule.

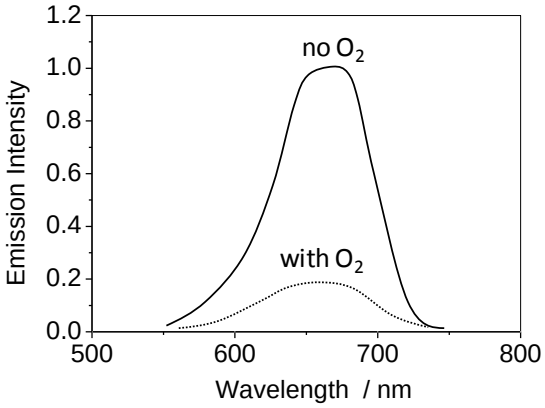
(6 marks)

ii) Derive the Stern-Volmer equation for bimolecular quenching defining all the terms used.

(4 marks)

iii) The emission from a ruthenium complex (RuX_3) is quenched by molecular oxygen in solution as illustrated in the figure 1. Assuming a diffusion-controlled rate constant of $k_Q = 10^{10}$ $M^{-1}s^{-1}$ and an excited state lifetime (of RuX_3) of 25μs, estimate the oxygen concentration in the solution.

(4 marks)



iv) Briefly explain why ruthenium complexes are used for the initiation of photochemical reactions in solution.

(2 marks)

QUESTION CONTINUED OVERLEAF

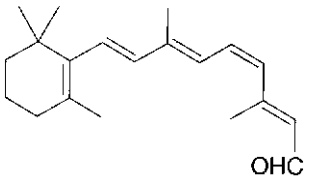
b) Answer **BOTH** parts of this question.

i) Photodissociation can result in the quenching of light emission. For optical excitation below its dissociation limit, a molecule exhibits an emission quantum yield of 0.77. When excited above its dissociation limit, the emission yield is found to decrease to 0.12. From this data estimate the quantum yield of photodissociation when exciting above the dissociation limit.

(3 marks)

ii) The figure below gives the structure of 11-cis-retinal. Detail the function of this molecule in the process of vision. Your answer should include a discussion of the process of photoisomerization in asymmetric alkenes.

(6 marks)



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

i) A dye used in solar cells has a fluorescence quantum yield of 0.63 in solution. When the dye molecule is covalently bound to the surface of TiO_2 the fluorescence quantum yield of the dye decreased to 0.15. From these data estimate the yield of photochemistry. Assuming $k_o = 3 \times 10^8\ s^{-1}$ for the dye what is the rate constant for photochemistry?

(6 marks)

ii) Give the equation for Fermi's Golden Rule, defining all terms used.

(3 marks)