

**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – MAY 2012, 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 IIIB**

**Paper 3**

**Friday 11<sup>th</sup> May 2012, 14:00-17:00**

**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.**

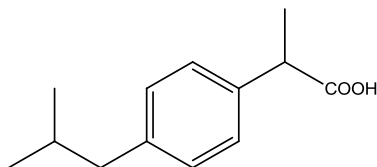
### 3.I8 – Solvents and Solvent Effects

Answer parts a), b) **AND** c) and **ANY TWO** of parts d)-f) of this question.

- a) Ibuprofen is a common anti-inflammatory agent. The final purification step for this compound involves liquid chromatography elution through a non-polar column. Match each solvent below with the respective retention time.

**Solvents:** acetone, acetonitrile, *n*-hexane, methanol, toluene, water

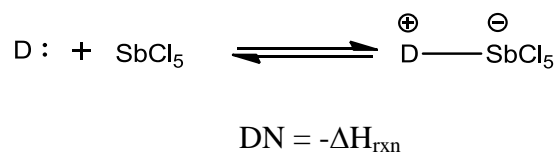
**Retention time (minutes):** 1.75, 1.92, 2.78, 3.10, 6.25, 29.00



**Ibuprofen**

(3 marks)

- b) The Gutmann Donor Number (DN) is a measure of the enthalpy of reaction between a solvent and antimony pentachloride:



Answer **ALL** parts of this question.

- i) Which of the three solvents diethylether, phenylmethylether and hexamethyldisiloxane will have the largest DN?

(1 mark)

- ii) Which of the three solvents diethylether, phenylmethylether and hexamethyldisiloxane will have the smallest DN?

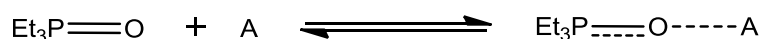
(1 mark)

- iii) If we defined  $\text{DN} = -\Delta G_{\text{rxn}}$  instead of  $\text{DN} = -\Delta H_{\text{rxn}}$ , which of the three solvents diethylether, phenylmethylether and hexamethyldisiloxane would see the largest change in DN? Briefly explain your answer.

(1 mark)

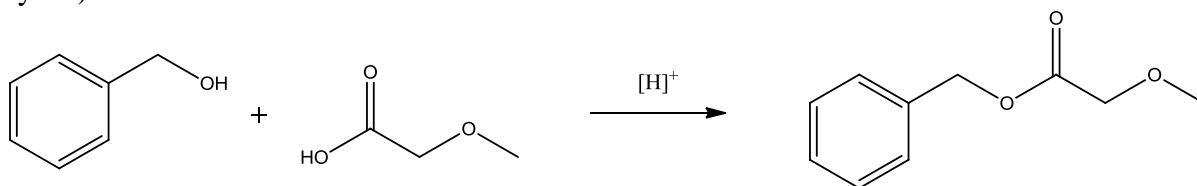
QUESTION CONTINUED OVERLEAF

- c) The Gutmann Acceptor Number (AN) is defined by the  $^{31}\text{P}$  NMR chemical shift of triethylphosphane oxide in various solvents.



Answer **ALL** parts of this question.

- How do solvents affect the  $^{31}\text{P}$  NMR shift of triethylphosphane oxide? (1 mark)
  - Will hydrogen bond donor solvents increase or decrease the  $^{31}\text{P}$  NMR shift of triethylphosphane oxide? Briefly explain your answer. (1 mark)
  - The  $^{31}\text{P}$  NMR shift of triethylphosphane oxide in dichloromethane is more positive than the shift in dimethylsulfoxide. Briefly explain this. (1 mark)
- d) The esterification reaction shown below is known to proceed through an  $\text{A}_{\text{AC}}2$  (acid-catalyzed) mechanism.



Solvent	$\alpha$	$\beta$	$\pi^*$	$k_2 (\text{h}^{-1} \text{M}^{-1})$
Acetonitrile	0.19	0.66	0.66	12.5
Acetone	0.08	0.48	0.71	24.5
Ionic Liquid	0.60	0.21	1.01	67.5
Tetrahydrofuran	0	0.55	0.55	18.9
Toluene	0	0.09	0.56	106.0

Rate data were obtained in various solvents, and it was discovered that the reaction rate constant depended solely on the Kamlet-Taft  $\beta$  parameter.

Answer **ALL** parts of this question.

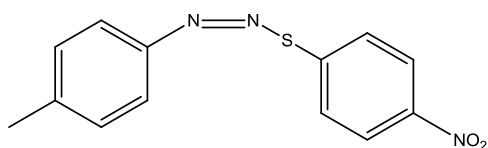
- Obtain an LSER relationship that will predict the rate of this reaction in various solvents. (3 marks)
- Predict the rate of reaction in cyclohexane ( $\alpha=0$ ,  $\beta=0$ ,  $\pi^*=0$ ) and in isopropanol ( $\alpha=0.76$ ,  $\beta=0.95$ ,  $\pi^*=0.48$ ). (2 marks)

QUESTION CONTINUED OVERLEAF

iii) Propose a role for an acid catalyst in the first step of this reaction mechanism.  
(1 mark)

iv) Describe what specific interaction(s) within the first step of the reaction mechanism are being affected by  $\beta$ . How is this contributing to the observed effect of  $\beta$  on the rate of reaction?  
(2 marks)

e) The solvent-mediated thermolysis of (*Z*)-benzenediazoalkyl sulfides (an example structure is shown below) can proceed through either homolytic bond cleavage (leading to *Z/E*-isomerization) or heterolytic bond cleavage (leading to decomposition). The relative rates of the decomposition : isomerization product formation are strongly solvent dependant.



Solvent	$k_1^{\text{decomp}} / k_1^{\text{isom}}$
Iso-octane	0.60
Benzene	1
Pyridine	25
Acetic Acid	45
DMSO	100
EtOH	190

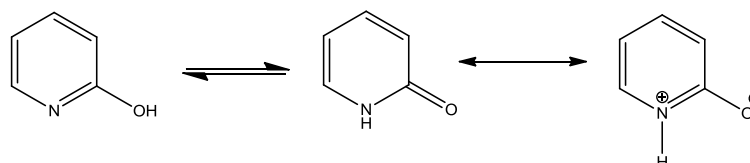
Answer **ALL** parts of this question.

i) Propose a transition state structure for both the homolytic bond cleavage and the heterolytic bond cleavage.  
(3 marks)

ii) Interpret the solvent effect on the relative rate data for these reactions.  
(5 marks)

QUESTION CONTINUED OVERLEAF

- f) The lactam/lactim tautomerization is strongly solvent dependant, with equilibrium constants ( $K_T$ ) varying from the gas phase to the solution phase by a factor of 10,000. Data are shown for the tautomerization of 2-hydroxypyridine.



Solvent	$K_T$
Gas phase	0.4
Cyclohexane	1.7
Chloroform	6.0
Acetonitrile	148.0
Water	910.0

Answer **ALL** parts of this question.

- Explain the solvent effect on the equilibrium position. (2 marks)
- Draw ONE DIAGRAM showing the reaction free energy for this reaction in both the gas phase and water. Clearly label every  $\Delta G$ . (5 marks)
- When the tautomerization of 4-hydroxypyridine is measured instead of 2-hydroxypyridine, the equilibrium constant in water increases to 1900 (from 910). Explain this result. (1 mark)

### 3.05 – Reactive Intermediates 2

Answer **ALL** parts of this question.

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

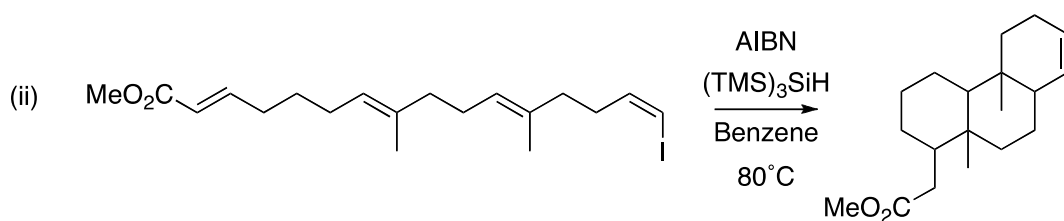
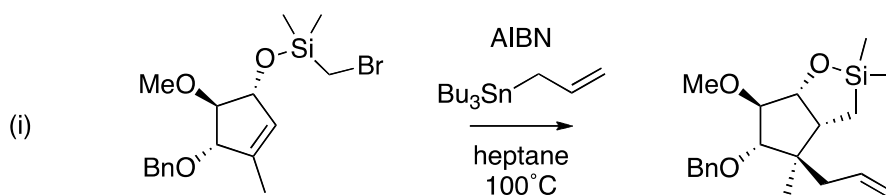
- i) Describe all the mechanistic steps that can occur in the reduction of an alkyl halide by tributyltin hydride.

(6 marks)

- ii) By consideration of the rate equations that govern propagating and chain termination steps, and given that radical-radical recombination is diffusion controlled (*i.e.* rate constant of *ca.*  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), what is the required relationship between radical concentration and the rate constants of the propagating steps for successful reduction of an alkyl halide by tributyltin hydride?

(4 marks)

b) Provide a detailed, annotated mechanism for **ONE** of the transformations shown below commenting on all aspects of selectivity.



(15 marks)

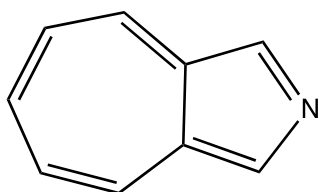
### 3.O10 – Molecular Modelling

Answer any **TWO** of the three parts a) – c) of this question.

a) Briefly discuss the following aspects of the molecular mechanics method:

- i) Why the mechanics method is not capable of studying the kinetics of reactions.  
(4 marks)
- ii) What attributes of the mechanics method as implemented in standard programs make it both more and less suitable for studying the geometry and free energy of host/guest molecular complexes.  
(4 marks)
- iii) The characteristics of the method for studying systems with diverse types of hydrogen bonding interactions, including in your discussion two examples.  
(4.5 marks)

b) The unusual heteroaromatic molecule aza-azulene **1** has been synthesized, but its characteristics towards electrophilic aromatic substitution reactions are unknown. Describe how you might go about predicting this reactivity, using nitrosyl-trifluoroacetate ( $\text{CF}_3\text{CO}_2\text{NO}$ ) as your reagent, and how you might modify your approach to include nucleophilic aromatic substitution. Include in your answer three different techniques for investigating the various possible regiochemical outcomes.  
(4 marks per technique + 0.5)

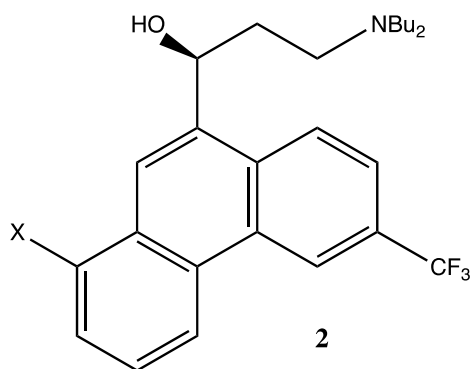


**1**

QUESTION CONTINUED OVERLEAF

- c) Structure **2** is the general form of a series of putative anti-malarial drugs known as halofantrines. When substituent  $X = H$ , resolution of **2** from its racemate on a chiral HPLC column is completely inhibited, whereas with  $X = Cl$ , such resolution is very facile. Describe how you might go about using modelling techniques to cast light on this unusual feature, including in your answer **three** methods based on analysing the calculated wavefunction of either a single molecule of **2**, or of any intermolecular dimer that might form, and including any aspect arising out of the antiperiplanar relationship between group  $X$  and the  $CF_3$  group.

(4 marks per technique + 0.5)





### 3.P6 – Molecular Electronic Materials

**ALL** answers should be expressed in **SI units**

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

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

- i) At what voltage in the operating range ( $0 < V < V_{oc}$ ) is the maximum photocurrent obtained from an organic solar cell? Explain your answer. (2 marks)
- ii) Provide a definition of the fill-factor and explain why it is desirable that the fill factor should be as close to unity as possible. (2 marks)
- iii) A single layer polymer solar cell is fabricated by sandwiching a poly-3-hexylthiophene film between two charge collecting electrodes. The device is illuminated by monochromatic light of 475 nm wavelength with an intensity of  $18 \text{ mWcm}^{-2}$ . It is found that 60% of the photo-generated charges undergo charge recombination. Estimate the maximum theoretical photocurrent the device can deliver under these conditions. Comment on your answer. State clearly any assumptions in your calculation. (4 marks)
- iv) State using appropriate diagrams to illustrate your answer the maximum photovoltage that can be extracted from an organic solar cell. (3 marks)
- v) What are the design criteria for improving the power conversion efficiency of two-component organic solar cells? (5 marks)

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

- i) Explain why transition metal complexes are considered favourable dopants for organic light emitting diodes. What potential limitation on device performance do they circumvent? (3 marks)
- ii) Briefly describe the two non-radiative energy transfer mechanisms by which excitons can move from a host semiconductor to a dopant molecule. (4 marks)
- iii) What is the dominant means of energy transfer for emissive molecules in low concentration solutions? (2 marks)

QUESTION CONTINUED OVERLEAF

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

- i) The photoluminescence quantum efficiency of a semiconductor is 25 % and the fluorescence lifetime is 1ns. What is the radiative lifetime?

(2 marks)

- ii) If the fluorescence quantum yield of a polymer is 75% what is the maximum efficiency achievable in an organic light emitting diode? State clearly any assumptions in your calculation.

(4 marks)

- iii) Define the following terms:

- a. Exciton
- b. Polaron
- c. Charge carrier mobility

(3 marks)

### 3.P10 – Soft Condensed Matter

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

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

- i) Estimate the Young's modulus of an Argon crystal and a crystal made of colloids of 1 micrometer diameter. Which crystal would be softer?

You may assume the pair interaction between colloids is 10 times stronger than the interaction between Argon atoms.

(3 marks)

- ii) Sketch the dependence of the mean square displacement with time of one water molecule in the liquid phase. Clearly identify in your plot the regions corresponding to ballistic and diffusive behaviours. Briefly explain the physical origin of the ballistic behavior.

(2 marks)

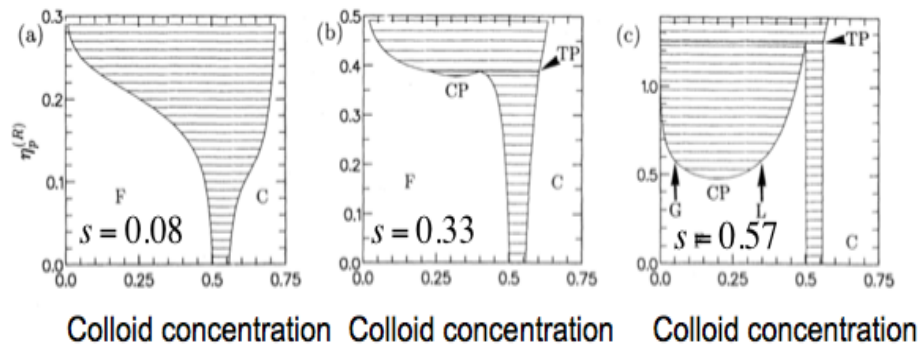
- iii) The mean square displacement scales with time as  $t^n$  in the ballistic regime. Use an appropriate derivation to calculate the exponent  $n$ .

(5 marks)

- iv) The figure below shows the phase diagram of a polymer colloid mixture, where  $s$  is the polymer to colloid diameter ratio. Assuming both the colloid and polymers behave like hard spheres, explain the physical origin of these diagrams. In your response you should make reference to the effect that the addition of polymer has on the effective interactions between the colloids.

Note: F, C, L and G, indicate fluid, crystal, liquid and gas

(5 marks)



QUESTION CONTINUED OVERLEAF

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

- i) A binary mixture undergoes a liquid-liquid transition at 400 K. Using mean field theory, estimate the composition of the mixture on the spinodal line.

Data:  $\frac{DF}{k_B T} = C x_a x_b + x_a \ln x_a + x_b \ln x_b$ ,  $C T = 1000$

(5 marks)

- ii) Use mean field theory to determine whether water and a liquid consisting of alkane molecules mix at 300 K.

Data:  $C T = 2000$ ,  $x_{\text{oil}} = 0.2$

(2 marks)

- iii) In the context of mean field theory, how is the parameter  $C$  related to the intermolecular interactions? What are the main approximations used to derive this relationship? Under what conditions does this approximation become inaccurate?

(3 marks)

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

- i) Consider a polymer solution. What is the *theta* temperature? Briefly explain how the polymer radius scales with the number of monomers below and above this temperature.

(2 marks)

- ii) Show that at the *theta* temperature the polymer end to end distance scales as  $r = a N^{1/2}$ , where  $N$  is the number of bonds and  $a$  the monomer-monomer distance.

(5 marks)

- iii) A molecular motor can produce up to  $10^{-20}$  J of work. Would this work be enough to stretch a single fragment of DNA from its undeformed end to end distance, 1 micrometer, to 3 micrometers, at 300 K?

You can assume the DNA can be modeled as a freely jointed chain.

(3 marks)