IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – JANUARY 2017, for Internal Students of the Imperial College of Science, Technology and Medicine

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

CHEM60001 ADVANCED CHEMISTRY

Paper 2

Thursday 12th January 2017, 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.

Q1: Materials Chemistry

Answer part a) **AND** part b) of this question.

a) Define three types of fundamental point defects. Explain why they frequently occur in pairs, distinguishing between a Frenkel and Schottky defect. Describe one technique that might be applied to characterise point defects and outline what information could be gained.

(10 marks)

b) Answer **THREE** of the following **FOUR** parts of this question.

i) AgCl is a silver ion conductor, through the formation of Frenkel defects. Identify, with justification, the likely conduction mechanism. What is likely to happen to the silver ion conductivity if the system is doped with $CdCl_2$?

ii) By analogy to an antiferromagnetic material, suggest what behaviour might be observed for a material termed *antiferroelectric*.

iii) Name and describe two mechanisms, one thermodynamically-driven and one kinetically-driven, through which Zeolite X could in principle be used to separate O_2 and N_2. Name another industrial application of zeolites that makes use of one of these mechanisms.

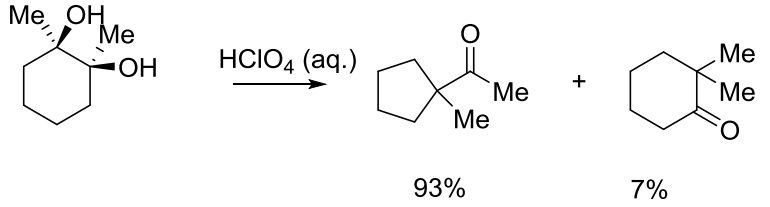
iv) Identify and describe a suitable characterisation technique for determining the oxidation state of copper in a $Cu/ZnO/Al_2O_3$ catalyst for methanol synthesis. What limitation might there be to the information obtained about the copper?

(5 marks for each part)

Q2: An Introduction to Reaction Stereoelectronics

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

a) The *cis*-diol shown below reacts in aqueous acid to give two products, as shown:



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i) Draw mechanisms for the formation of each product.

(4 marks)

ii) Highlight the key bonds that are involved in each reaction. Explicitly indicate which orbitals are involved and their relative orientations.

(5 marks)

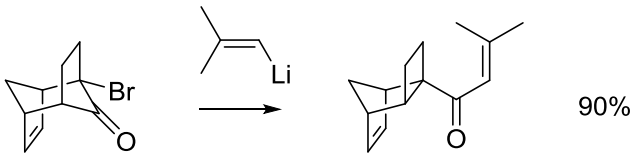
iii) Provide possible reasons as to why the cyclopentane is the major product.

(3 marks)

iv) Would you expect the isomeric *trans*-1,2-diol substrate to give the same products? Explain.

(4 marks)

b) Consider the following reaction which is a key step in Harmata's approach to tricyclolavulone.



i) Draw a mechanism for the formation of the product.

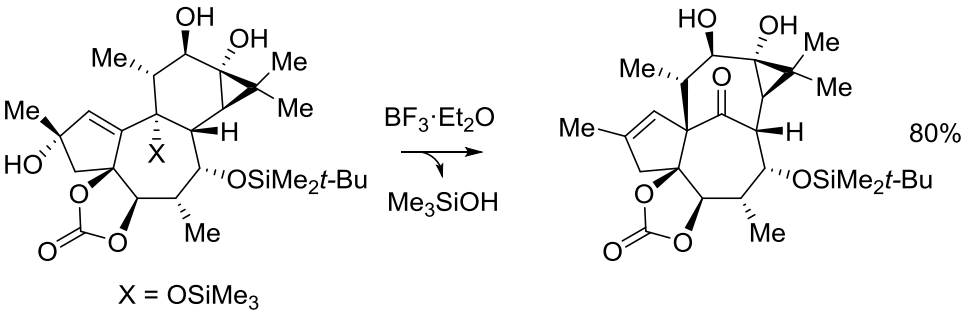
(4 marks)

ii) Highlight the key bonds that are involved in this reaction and explicitly indicate which orbitals are involved and their relative orientations.

(5 marks)

QUESTION CONTINUED OVERLEAF

c) Consider the following reaction which is a key step in Baran's synthesis of ingenol.



X = $OSiMe_3$

i) Draw a mechanism for the formation of the product. HINT: The Lewis acid initiates this reaction by interacting with the allylic alcohol.

(4 marks)

ii) Highlight the key bonds that are involved in this reaction. Explicitly indicate which orbitals are involved in the reaction and their relative orientations.

(5 marks)

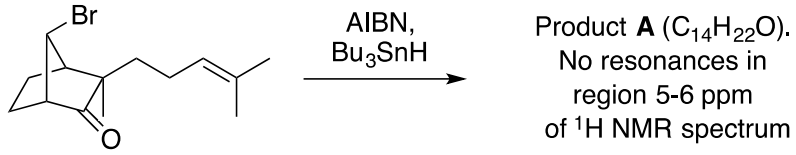
Q3: Reactive Intermediates

Answer part a) **AND** either part b) **OR** part c) of this question.

a) Compare and contrast the requirements for intermolecular versus intramolecular carbon-carbon bond formation via the addition of a carbon-centred radical to an alkene.

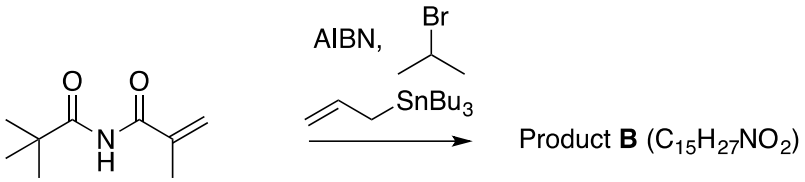
(10 marks)

b) Predict the major product **A** for the reaction shown below, providing also an annotated curly arrow mechanism, commenting on any aspects of reactivity, selectivity and stereochemistry where appropriate.



(15 marks)

c) Predict the major product **B** for the reaction shown below, providing also an annotated curly arrow mechanism. Comment on any aspects of reactivity, selectivity and stereochemistry where appropriate.



(15 marks)

Q4: Statistical Thermodynamics

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

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

i) The ergodic hypothesis is one of the main postulates of Statistical Thermodynamics. Explain its significance, and provide one example of a system that does NOT fulfill this hypothesis.

(2 marks)

ii) What is the vibrational heat capacity of 1 mol of CO molecules in the gas phase?

Sketch and explain the general dependence of the vibrational heat capacity as a function of temperature.

(3 marks)

iii) Consider one CO_2 molecule adsorbed in a nanopore of volume 10 nm^3.

Would the classical approximation be an accurate approach to calculate the translational properties of the molecule?

m_C=12 g mol^{-1}; m_O=16 g mol^{-1}; T=300 K.

(5 marks)

iv) The residual entropy of a solid consisting of molecules with the chemical formula AB_nC_m is 14.9 J K^{-1} mol^{-1}. Find the full formula, i.e. *n* and *m*, of the molecule. Explain your assumptions.

You may consider that atoms *B* and *C* are bonded to *A*, with the latter being at the centre of mass of the molecule, and that $m+n=4$.

(5 marks)

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

Consider the vibrational partition function

$$q_v = \frac{\exp\left(\frac{-\theta_v}{2T}\right)}{1-\exp\left(\frac{-\theta_v}{T}\right)}$$

where

$$\theta_v = \frac{h\nu}{k_B}$$

QUESTION CONTINUED OVERLEAF

i) Show that the statistical thermodynamic equation for the vibrational internal energy of a gas of diatomic molecules is given by:

ii)

$$U^v = \frac{Nk_B\theta_v}{2} + Nk_B\theta_v \frac{\exp\left(-\frac{\theta_v}{T}\right)}{1-\exp\left(-\frac{\theta_v}{T}\right)}$$

(6 marks)

iii) State the limiting behavior of the vibrational energy at low and high temperatures. Briefly explain the physical meaning of your result.

(4 marks)

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

i) 1 mol of ideal gas at 298 K undergoes a reversible expansion and its volume changes from 1 cm^3 to 50 cm^3.

Using the statistical mechanics equation for the free energy in the canonical ensemble, calculate the work associated with the expansion of the gas. How much heat is exchanged in this process?

(5 marks)

ii) Consider the ionization of *K*, $K \rightleftharpoons K^+ + e^-$

Write the statistical thermodynamics equation for the equilibrium constant of the reaction in terms of the relevant partition functions.

Calculate the *electronic partition* functions of the reactants and products.

(5 marks)