IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 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 3

Tuesday 07th May 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.I1 – Inorganic Mechanisms and Catalysis

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

a) The reductive elimination and oxidative addition of H_2, R-H and R-R (where R is an alkyl group), at transition metal centres typically results in an equilibrium, as illustrated. Given the bond dissociation energies (BDE's) below, explain the position of the equilibria.
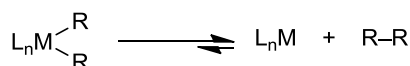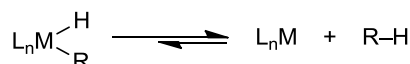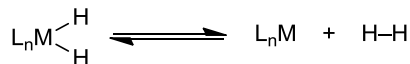
BDE (H–H) = 104 kcal/mol
BDE (M–H) = 50-60 kcal/mol
BDE (R–H) = 97-101 kcal/mol
BDE (M–R) = 30-40 kcal/mol
BDE (R–R) = 83-85 kcal/mol

(5 marks)

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

   i) The rhodium-catalysed carbonylation of ethanol results in the formation of propionic acid (see below). Draw a catalytic cycle that explains this reaction. The analogous reaction with n-propanol results in the formation of two isomeric products: butyric acid and iso-butyric acid, as shown below. Explain this observation.
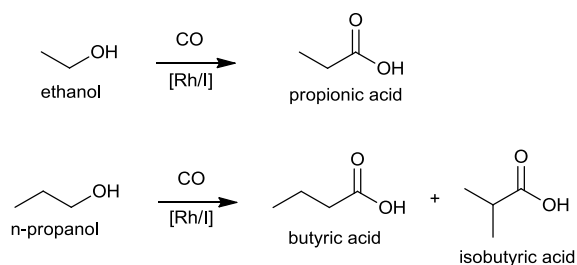
(9 marks)

ii) The relative rates of nucleophilic substitution reactions for the following alkyl iodides are given below. Explain how this will affect the rate of carbonylation for methanol, ethanol and n-propanol.

Methyl iodide: 30
Ethyl iodide: 1
n-Propyl iodide: 0.4

(3 marks)

c) The hydrosilylation of ethene is catalysed by Pt(0) complexes, for example [Pt(PPh$_3$)$_4$], as shown below. In addition to the expected product, the formation of two byproducts, ethane and a vinylsilane, is observed in a 1:1 ratio. Draw the catalytic cycle for this reaction and explain the formation of the byproducts.

$$HSiR_3 \quad + \quad C_2H_4 \quad \xrightarrow{\text{Pt(0)}} \quad H_3CCH_2SiR_3 \quad (+ \quad C_2H_6 \quad + \quad H_2C=CHSiR_3)$$

(8 marks)

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

i) Nylon-6,6 is a polyamide polymer made from adipic acid (see below) and 1,6-diaminohexane. Describe two industrial routes for the preparation of adipic acid starting from 1) cyclohexane and 2) butadiene. In the case of butadiene, draw a catalytic cycle to explain the reaction mechanism.

ii) How does nylon-6,6 differ structurally from nylon-6, prepared by the ring opening polymerization of ε-caprolactam (see below)?
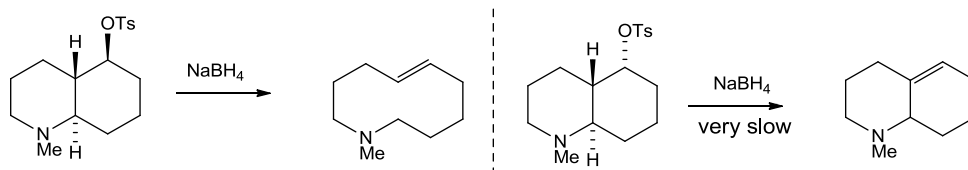
(8 marks)

adipic acid

ε-caprolactam
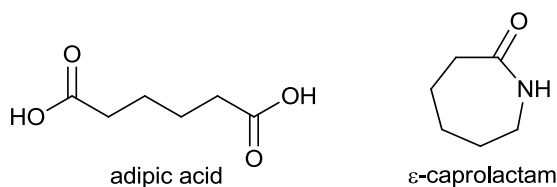
3.O12 – An Introduction to Reaction Stereoelectronics

Answer **BOTH** parts of this question.

a) Shown below are contrasting reactions of two diastereomeric tosylates under identical conditions.


   i) Draw mechanisms for both transformations.

(3 marks)

   ii) Explain the contrasting behaviour. Include in your answer diagrams of the two reactions with the key bonds highlighted, and show the key orbitals that are involved.
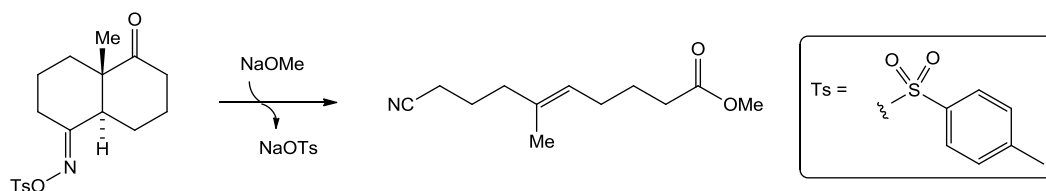
(7 marks)

b) Give a mechanism for **THREE** of the **FIVE** following transformations. For each mechanism, also highlight the key bonds and show the key orbitals that are involved.
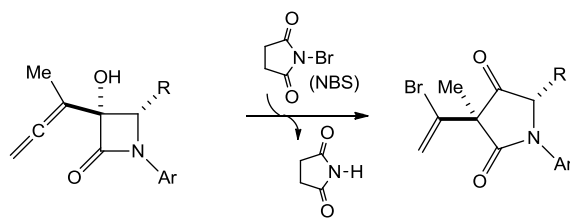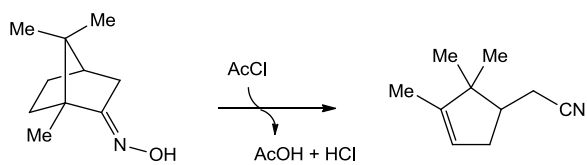
   i)

(5 marks)

   ii)
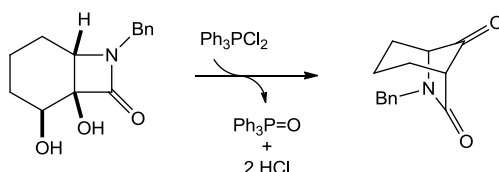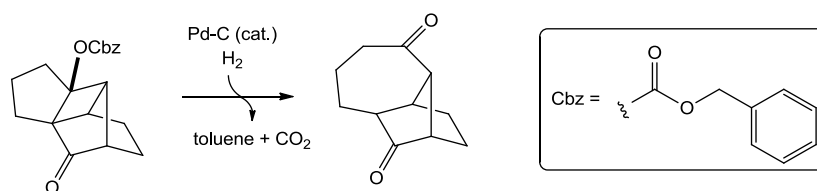

(5 marks)

iii)

(5 marks)

iv)

(5 marks)

v)

(5 marks)

3.P11 – Statistical Thermodynamics

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

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

    i) State the ergodic hypothesis. Give one example of a system that violates this hypothesis.

        (1.5 marks)

    ii) Low temperature experiments of a crystal consisting of triangular molecule AB_2C show that the crystal entropy does not converge to zero as the system approaches 0 K. Explain this observation and estimate the molar entropy.
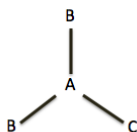
        (4 marks)

    iii) Calculate the number of accessible rotational energy levels for 1 molecule of O_2 at 300 K.

        Data: Atomic mass of Oxygen = 16 g/mol; O_2 bond length = 0.121 nm

        (4 marks)

    iv) The ground electronic state of nitrogen monoxide consists of two doubly degenerate energy levels (see figure below). Derive the canonical ensemble expression of the internal energy for N electrons.

        Hint: you may assume that the particles are distinguishable

        (4 marks)

    v) For the two energy level system discussed in question iv) above, sketch the dependence of the internal energy on temperature, showing clearly the limiting behaviour as T→0 and as T→∞.

        (1.5 marks)

b) Statistical thermodynamics provides an exact equation for the vibrational partition function of the harmonic oscillator.

   i) Show that the vibrational partition function is given by:

$$q^v = \frac{\exp(-q_V/(2T))}{1 - \exp(-q_v/T)}$$

Hint: you may want to consider the energy of the harmonic oscillator:

$$u_n = \left(n + \frac{1}{2}\right)h\nu \text{ and } q_v = \frac{h\nu}{k_B}$$

(5 marks)

   ii) Estimate the number of vibrational energy levels that one oxygen molecule can access at 2000 K.

Data: $m(O) = 16$; $\nu(O_2) = 1580$ cm^{-1}

(3 marks)

   iii) Using the equipartition theorem estimate the total heat capacity of 1 mol of O_2 in the gas phase at 1000 K. Compare your result with the experimental one and explain the difference.

Data: Experimental heat capacity of O_2 at 1000 K and 1 bar: 26.56 J K^{-1} mol^{-1}

(2 marks)

c) The Sackur-Tetrode equation provides a route to calculate the absolute entropy of atomic gases.

   i) Derive the molar translational entropy of an ideal gas (Sackur-Tetrode equation) in the canonical ensemble. Clearly show your working and the approximations used in your derivation.

(5 marks)

   ii) Show that the "translational" contribution to the entropy of 1 mol of CO_2 molecules in the gas phase at 10^5 Pa and 300 K is 156.2 J K^{-1} mol^{-1}.

  Data: Atomic mass of C $=12$ g/mol, O$=16$ g/mol.

(3.5 marks)

iii) The experimental estimate for the "total" entropy of gaseous CO_2 at 300 K is 213.8 J K^{-1} mol^{-1}. Briefly explain the physical origin of the difference between this value and the value of the translational entropy estimated in part ii) above.

What extra information would be needed to obtain an accurate statistical mechanics estimate of the total translational entropy of CO_2?

(1.5 mark)

List of useful equations

$$q^t = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

$$q^r = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

$$S = \frac{5R}{2} + N k_B \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{RT}{N_A P} \right]$$