IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 2014, 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 06th May 2014, 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) Answer **BOTH** parts of this question.

i) Draw a catalytic cycle for the hydrogenation of ethene using Wilkinson's catalyst. Given that the oxidative addition of H_2 is the rate-determining step, provide a rate equation that describes the overall hydrogenation reaction.

(8 marks)

ii) A study on the effect of different ligands has shown the following reactivity order:

Ligand:	*Relative reactivity:*
$(4\text{-}ClC_6H_4)_3P$	1.7
$(C_6H_5)_3P$	41
$(4\text{-}CH_3C_6H_4)_3P$	86
$(4\text{-}CH_3OC_6H_4)_3P$	100

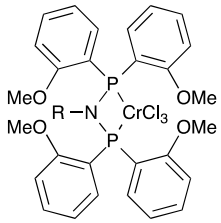
Explain this reactivity order.

(4 marks)

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

i) The chromium-catalysed selective trimerisation of ethene to give 1-hexene occurs via a metallacyclic mechanism. Give the mechanism for this reaction, starting from a $[(PNP)Cr^{I}]$ species, which is generated from the $[(PNP)CrCl_3]$ complex shown below and methylaluminoxane (MAO).

(4 marks)

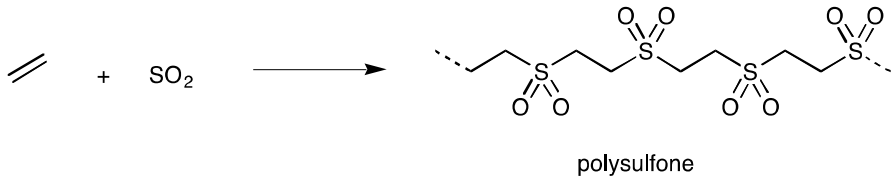


ii) The selectivity of the oligomerisation reaction can be changed to produce 1-octene, when a different ligand is used, that does not contain the *ortho*-methoxy groups on the phenyl substituents of the ligand AND when higher ethene pressures are used. Explain this observation.

(4 marks)

QUESTION CONTINUED OVERLEAF

c) Polysulfone may be prepared from ethene and SO_2 using a metal catalyst. Suggest a suitable metal for this reaction, draw a potential catalytic cycle for this process and explain the individual steps.



(5 marks)

d) Using energy diagrams illustrate the difference between a catalysed and an uncatalysed reaction in terms of both kinetics and thermodynamics. With reference to these diagrams, explain what is meant by the active species, the resting state and the rate-determining step in a catalytic cycle.

(5 marks)

3.O3 – Fundamentals of Polymer Chemistry

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

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

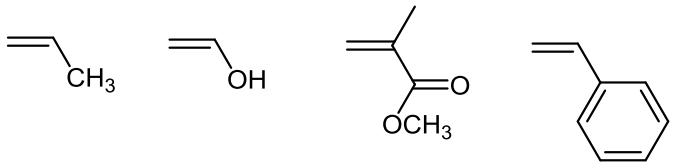
i) Draw the structure of syndiotactic polystyrene – including any stereochemistry.

(2 marks)

ii) Explain the effect on molecular weight of increasing the temperature of a free radical solution polymerisation.

(2 marks)

iii) Match the following four vinyl monomers with the appropriate efficient initiator or catalyst 1-4) for polymerisation.



A B C D

1) AIBN, 2) none possible, 3)$TiCl_4/Al(CH_3)_3$, 4)PhMgBr

(4 marks)

iv) Three monodisperse polymers of the same structure, A, B and C, have molar masses of $1.5x10^4$, $2.5x10^5$ and $4.0x10^5$ g mol^{-1}, respectively. Calculate the number-average and weight-average molecular weights of a polymer prepared by mixing A, B and C in weight ratios of A:B:C = 1:2:3.?

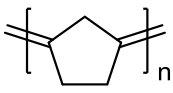
(4 marks)

v) Describe the differences in the rate of propagation and initiation between free radical polymerisation and controlled radical polymerisation.

(2 marks)

vi) Which CRP polymerisation process would be most suitable to synthesise the following?

a) Low molecular weight styrene block copolymers.
b) Metal free- high molecular weight poly(methyl methacrylate).
c) Poly(norbornene) (shown below).



(3 marks)

QUESTION CONTINUED OVERLEAF

vii) A condensation polymerisation of nylon-6 was found to have an extent of reaction (p) of 0.96. Calculate the number average molecular weight of this polymer.

(3 marks)

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

i) How does the concentration of the initiator and monomer influence the molecular weight in a solution chain growth polymerisation?

(2 marks)

ii) For the following 3 sets of monomer reactivity ratios, describe the nature of the resulting co-polymers.

A) r1 = 1.0; r2 = 1.0 B) r1 = 0.01; r2 = 0.01 C) r1 = 50; r2 = 0.01

(3 marks)

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

i) Draw the reaction mechanism for a chemically amplified resist system, including initial polymer structure and products.

(3 marks)

ii) Describe two molecular characteristics of a polymer used in a skin care emulsion

(2 marks)

3.P3 – Molecular Reaction Dynamics

Answer any **TWO** of the three parts a), b) and c) of this question.

There is an attached sheet of equations that you may find useful.

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

i) Draw a potential energy diagram to explain the effect that solvent may have on I_2 dissociation following excitation with a short laser pulse. Use your sketch to justify why an experiment monitoring the concentration of I_2 might appear to oscillate with time.

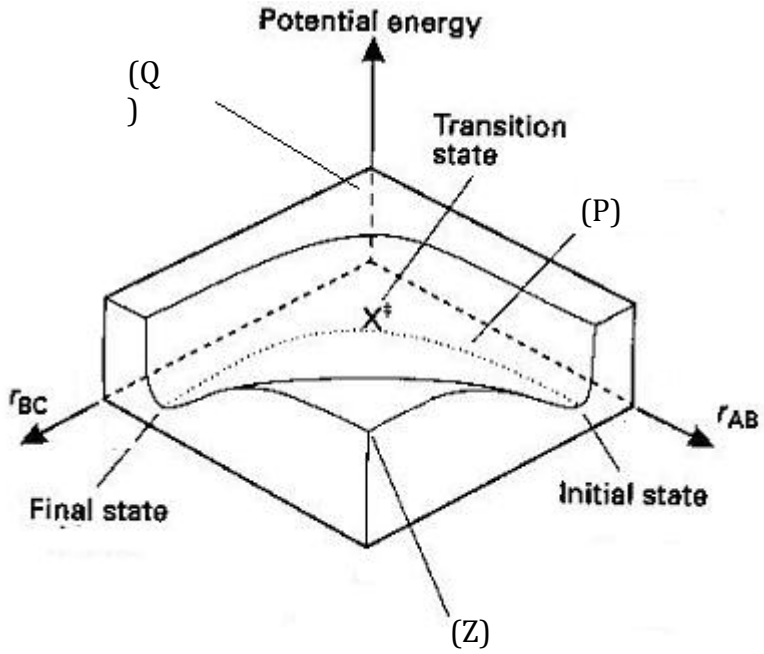
(6 marks)

ii) Consider the dissociation of hydrogen on a metal surface. Explain why the zero point energy of reactants and products needs to be taken into account, and explain how this may affect the rate of the reaction.

(6.5 marks)

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

i) The potential energy surface below is describing a three body interaction that occurs following a collinear collision of the form A + BC → AB + C.



QUESTION CONTINUED OVERLEAF

A. Describe what is represented by the dotted line labelled (P)
B. Describe what is represented by the high energy states labelled (Q) and (Z)
C. Describe the shape of the potential energy profile along the r_{BC} coordinate when r_{AB} is large.

(5 marks)

ii) A diatomic molecule is involved in an in-line collision with an ion. Discuss and explain in terms of classical mechanics why the reaction might be more efficient when the diatomic molecule is in a vibrationally excited state than when it is in a ground vibrational state, even if the total energy of the system remains the same in both cases. Use drawings of 2D potential energy surfaces to explain this observation.

(7.5 marks)

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

i) The rate of electron transfer between an electron acceptor and electron donor embedded in a protein is found to be 5.5×10^{8} s^{-1}. Assuming activationless electron transfer and an electron tunnelling coefficient of 1.4 $Å^{-1}$, calculate the edge to edge distance between the acceptor and donor. Explain your working and define each symbol used.

(6.5 marks)

ii) Derive the relationship between equilibrium constant and the degeneracies of the reactant and product states, with reference to the entropy difference between the reactant and product states. Define all symbols used. Use this to explain how the number of energy levels accessible to reactants and products affects a chemical equilibrium.

(6 marks)