**IMPERIAL COLLEGE LONDON**

**BSc and MSci DEGREES – JANUARY 2015, for Internal Students of the Imperial College of Science, Technology and Medicine**

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

# 1A PAPER ONE

**Monday 12th January 2015, 14:00-16:15**

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

## 1.I4 –Atomic Structure

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

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

i) Explain why the electron affinity of Cl is larger than F.

(2 marks)

ii) State two ways in which the Schrodinger model of the hydrogen atom differs from that of the Bohr model.

(2 marks)

iii) Using the Rydberg equation, calculate the initial energy level when an electron in a hydrogen atom transitions to n = 2 and emits a photon of wavelength 410.1 nm.

(4 marks)

iv) Put the following three ions in order of increasing size (smallest first) and explain your reasoning:

the phosphide ion, $P^{3-}$; the sulfide ion, $S^{2-}$; the chloride ion, $Cl^{-}$

(4 marks)

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

i) Suggest the ground state electron configuration of element 109, meitnerium.

(4 marks)

ii) There is no g block in the Periodic Table as no elements with outer electrons in g orbitals exist in nature or have been made artificially. Suggest a minimum atomic number for such an element.

(3 marks)

c) Using Slater's Rules, calculate $Z_{eff}$ for a 6s or a 5f electron in platinum. State which electronic configuration is more stable, and comment on the usefulness of the Rules.

(6 marks)

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

i) Sketch a graph for the first ionisation energies of the elements sodium to argon and explain any variations within the series.

(3 marks)

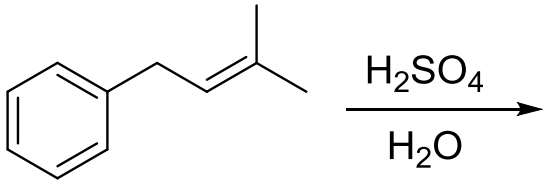
ii) Aluminium oxide, $Al_2O_3$, has a high melting point and it reacts with both hydrochloric acid and sodium hydroxide. What information can be deduced about the chemical nature of aluminium oxide from this information?

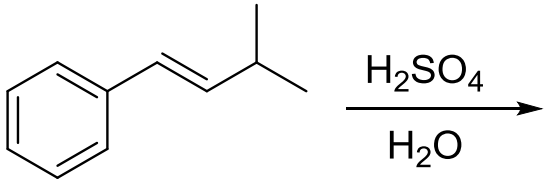
(3 marks)

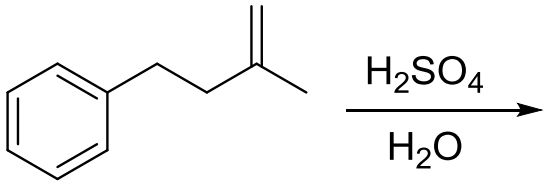
## 1.O2 – Alkanes, Alkenes & Alkynes

Answer **ALL** parts of this question.

a) For **EACH** of the following reactions identify the major product formed, providing a complete mechanism and rationale for the formation of this product.

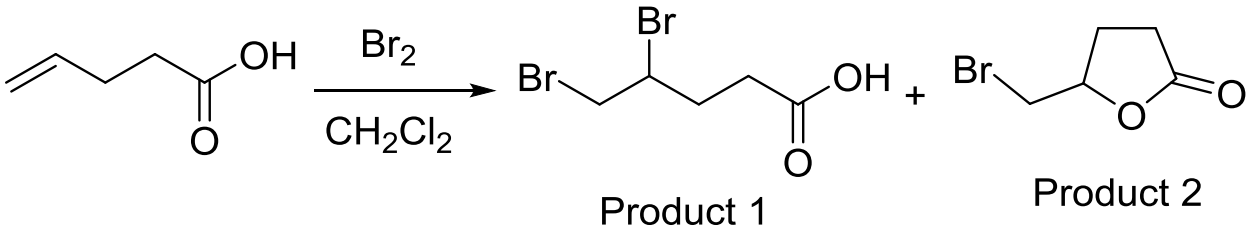
i) 


ii) 


iii) 


(10 marks)

b) Account for the formation of the two products in the reaction below, providing a full mechanism for the formation of each, identifying key intermediates where appropriate.




Product 1 Product 2

1 : 1 mixture of products

(6 marks)

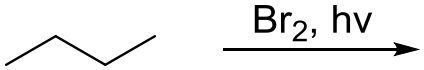
QUESTION CONTINUED OVERLEAF

c) How would you convert Product 1 to Product 2?

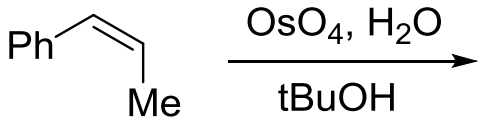
(1 mark)

d) Identify the major product formed in **TWO** of the following transformations. Provide full mechanisms and give detailed explanations for any selectivity observed.

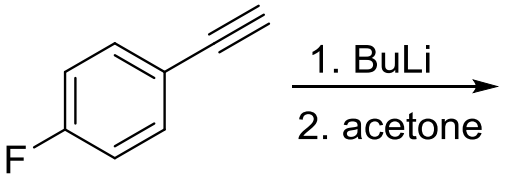
i)




ii)




iii)




(4 marks each)

## 1.P1 – Chemical Kinetics

Answer parts a)-d) and then **EITHER** part e) **OR** part f) of this question.

a) The Arrhenius equation states that $k=Ae^{-Ea/RT}$ where $k$ is the rate constant for the reaction, $A$ is the pre-exponential factor and $E_a$ is the activation energy. If only the temperature is varied, what are the maximum and minimum values that $k$ can take. Fully explain your answer.

(3 marks)

b) State which of the statements below are TRUE or FALSE. In each case fully justify your answer.

i) Catalysts speed up the rate of a given reaction in both the forward and backward directions.
ii) Catalysts favour the formation of products.
iii) The slowest step in a reaction scheme is the rate-determining step.

(6 marks)

c) The Lindemann-Hinshelwood mechanism states that

1. $A + A \rightarrow A^* + A$ (forward reaction rate = $k_1$; reverse reaction rate = $k_{-1}$)
2. $A^* \rightarrow P$ (forward reaction rate = $k_2$)

where A* is an activated reaction intermediate.

Comment on the effect of pressure upon the rate of reaction for the reverse reaction rate (step governed by $k_{-1}$) and the forward reaction rate (step governed by $k_2$).

(4 marks)

What are the limitations of the mechanism? How would you improve the model?

(3 marks)

d) Explain the difference between thermal and chain-branching explosions.

(3 marks)

QUESTION CONTINUED OVERLEAF

e) For the reaction:

$$A \rightarrow \text{Products}$$

it is shown experimentally that the rate law is such that:

$$\frac{d[A]}{dt} = -k[A]^2$$

By deriving and then using the integrated rate law for this system, show that the half-life of this system would be expected to vary with concentration.

(6 marks)

f) The Maxwell distribution of speeds is given by:

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-Mv^2/2RT}$$

where $M$ is the molar mass, $v$ is the speed, $R$ is the molar gas constant and $T$ is the temperature.

Starting from the equation for the Maxwell distribution of speeds, show that the average speed of molecules is given by:

$$\left(\frac{8RT}{\pi M}\right)^{1/2}$$

(6 marks)