

Eastern University, Sri Lanka

External Degree

First Year Second Semester Examination in Science

2004/2005 (January / March 2011)

EXTCH 104 Reaction Mechanisms and Chemical Kinetics

(Proper and Repeat)

Answer all questions

Time: One Hour

1. (a) Carbocation is one of the reactive intermediates in organic reactions

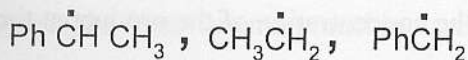
(i) Draw the "structure" of tertiary butyl carbocation

(15 marks)

(ii) Explain the various factors that contribute to the stability of the tertiary butyl carbocation with appropriate diagram(s)

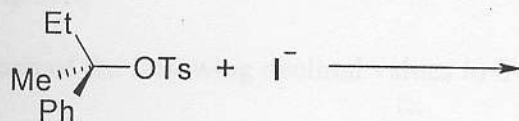
(20 marks)

(iii) Arrange the following free radicals in an increasing order of stability



(15 marks)

(b) (i) Give reason predict the product(s) formed in the following reaction.



(15 marks)

(ii) Write the rate expression for the reaction and explain the influence of I^- concentration on the rate of the reaction

(15 marks)

(iii) Draw a fully labelled energy profile diagram for the above mentioned reaction

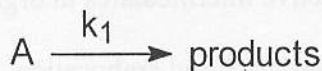
(20 marks)

cont...

2. (a) Write short notes on the followings

- (i) Order of a reaction (10 marks)
- (ii) Molecularity of a reaction (10 marks)
- (iii) Complex reaction (15 marks)
- (iv) Steady-state approximation (15 marks)

(b) Consider the following reaction which follows first order kinetics with respect to A.



- (i) Write down the first order rate expression for the above reaction and explain all the terms involved in it. (15 marks)
- (ii) Derive the integrated rate equation $k_1 = \frac{1}{t} \ln \left\{ \frac{a}{a-x} \right\}$ where 'a' is the initial concentration of A and 'x' is the concentration of the product at time "t". (20 marks)
- (iii) How would you determine the first order rate constant graphically? (15 marks)