Eastern University, Sri Lanka

First Year Second Semester Examination in Science

2007/2008 (August /September 2009)

CH 104 Organic reaction mechanism and chemical kinetics

Proper & Repeat

Time allowed: ONE HOUR

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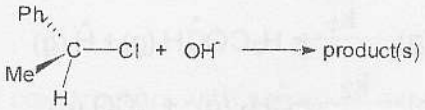
1. (a) Arrange the following radical intermediates in an increasing order of stability. Give reasons for your answer.

$(Me)_2\dot{C}H$, $\dot{C}H_3$, $(Me)_3\dot{C}$, $Me\dot{C}H_2$

20 marks

(b) Consider the following base hydrolysis reaction of alkyl halide.



(i) Write down all the products (with correct stereochemistry) formed in the above reaction.

(ii) Write down the rate equation for the reaction.

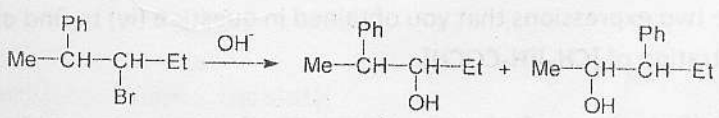
(iii) Draw the most plausible mechanism for the reaction and give reasons for your answer.

(iv) Draw a fully labeled energy profile diagram for the reaction.

(v) Explain the effects of polar solvents on the reactivity of the above reaction

(c) Explain the following observations. **40 marks**

(i)



20 marks

(ii) pK_a values of CH_3CH_2COOH, CH_2=CHCOOH and HC≡CCOOH are 4.88, 4.25 and 1.84 respectively **20 marks**

2. (a) Compare the order and molecularity of a reaction. **20 marks**

(b) Consider the following first order elementary reaction of the type

$$A \longrightarrow \text{products}$$

(i) Write down the rate expression with respect to A. Assume that the initial concentration of A is '***a***' mol.l^{-1} and '***x***' is the concentration of A reacted at time '***t***'.

(ii) Derive the integrated rate expression for the above reaction. Explain all the terms involved in it.

(iii) How would you determine the first order rate constant by a graphical method?

(iv) Show that the half-life of the reaction is independent of the initial concentration. **40 marks**

(c) Thermal decomposition of ethylene oxide occurs by the mechanism

Step I $H_2COCH_2\ (g) \xrightarrow{k_1} H_2C\dot{O}\dot{C}H\ (g) + \dot{H}\ (g)$

Step II $H_2C\dot{O}\dot{C}H\ (g) \xrightarrow{k_2} \dot{C}H_3\ (g) + CO\ (g)$

Step III $\dot{C}H_3\ (g) + H_2COCH_2\ (g) \xrightarrow{k_3} H_2C\dot{O}\dot{C}H\ (g) + CH_4\ (g)$

Step IV $\dot{C}H_3\ (g) + H_2C\dot{O}\dot{C}H\ (g) \xrightarrow{k_4}$ Products

(i) Identify the initiation, propagation and the termination step(s) from the above reaction sequence.

(ii) Write the expression for **d[products]/dt** from step **IV**.

(iii) Write expressions for **d[CH_3]/dt and d[CH_2OCH]/dt** from the reaction sequence.

(iv) Apply the steady state approximation for CH_3 and H_2COCH in question (iii).

(v) Add the two expressions that you obtained in question (iv) to find out the product concentration of **[CH_3][H_2COCH].**

(vi) Substitute the result that you obtained in the expression written question (ii) and show that

$$\frac{d[products]}{dt} = \frac{k_1[H_2COH_2]}{2}$$

40 marks