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Rajarata University of Sri Lanka
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RAJARATA UNIVERSITY OF SRI LANKA

FACULTY OF APPLIED SCIENCES

B.Sc. (Joint Major) Degree in Chemistry & Physics

Fourth Year Semester II Examination- October/November 2014

CHE 4204 PHOTOCHEMISTRY

Answer **ALL** questions **Time:** Two hours

A non programmable calculator is permitted

1.

(a) Write short notes on the following

(i) Forster theory of resonance energy transfer (ii) Fluoresence quenching

(b) Explain the following

(i) Fluoresence occurs only from lowest vibrational level of S_1

(ii) In some molecules Intersystem Crossing takes place with 100% efficiency

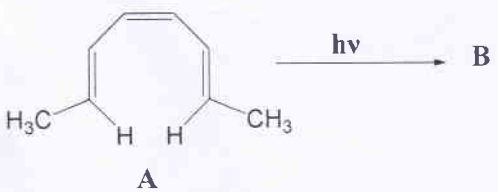
(iii) Radiation less conversion

(c) What is meant by Frank-Condon Principle?

(d) It was found in a photochemical experiment 307 J of energy decompose 1.30×10^{-3} moles of HI. Calculate the quantum yield of the reaction. Wavelength of radiation is 253.7 nm.

2.

(a) Draw molecular orbital view of excitation showing the nodes and electron distribution for trans-cis-trans octatriene (A) and give the structure of its photochemical product (B).

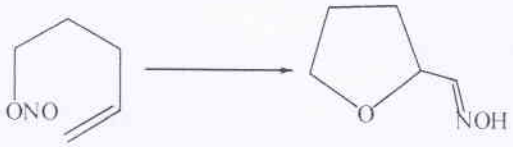


A

(b) Give probable mechanism for the following photochemical reaction

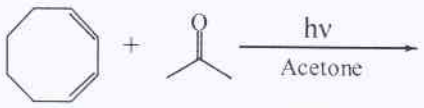
(i)

(ii)

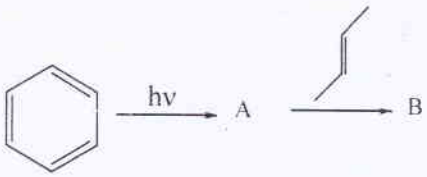


(c) Give the structure of product in each of the photochemical reaction

(i)



(ii)



3.

(a) Ground state molecular oxygen is triplet whereas electronically excited oxygen is singlet. Explain with a suitable molecular orbital diagram.

(b) Explain a photosensitization method of production of singlet oxygen and superoxide radical anion and briefly discuss the importance of singlet oxygen.

(c) Describe the photochemical reactions involve in the formation and depletion of ozone layer.

4.

(a) Simple photochemical reactions can be described by the following elementary kinetic steps

$$A + h\upsilon \xrightarrow{k_1} A^*$$

$$A^* + A \xrightarrow{k_2} A+A$$

$$A^* \xrightarrow{k_3} P$$

Rate of the first reaction = $k_1 I_0[A]$, where I_0 is the constant intensity of the light shining on the reaction mixture, and k_1 is the kinetic rate constant for this process.

(i) Write a differential rate equation for the rate of change of the intermediate species [A*] using this kinetic scheme.

(ii) Making appropriate approximations solve the equation in part (a) above for [A*].

(iii) When $k_2[A] >> k_3$, show that rate equation for the appearance of product, dP/dt, Which is independent of the concentration of A.?

(iv) Find an expression for quantum yield, ϕ in terms of rate constants and [A] using the information given at the beginning of this problem and the results of part (ii). Under what conditions does quantum yield, $\phi \rightarrow 1$?

(b) Give reasons for low quantum yield of many reactions