

2023

Time - 3 hours

Full Marks - 80

Answer ALL questions.

Figures in the right hand margin indicate marks.

1. (a) It is stated that only UV-visible region of light is able to produce chemical change, while others are not. Why? Give three examples of Naturally occurring photochemical reactions ? [10]
- (b) What are the factors to be considered during the determination of reaction mechanism of photochemical reactions? Give the schematic representation for the following types of reactions : (i) Photodissociation (ii) Photoaddition (iii) Photoisomerisation (iv) Photopolymerisation (v) Photooxidation (vi) Photoreduction. [4 + 6]

OR

- (a) State "Grotthus-Draper's Law" of photochemistry? Write notes on the following terms : (i) VC (ii) IC (iii) ISC. [10]
- (b) Give answer to the following questions : [5 × 2]
- (i) Calculate energy [in calories] associated with 1 mole of radiation of wavelength 2000 Å.

[2]

(ii) For the following photochemical reaction $A \xrightarrow{h\nu} B$ 1.0×10^{-5} mole of B was formed on absorption of 6.626×10^7 ergs of energy of radiation of wavelength 3600 Å. Calculate the quantum yield.

2. (a) Ketones mainly give four types of photochemical reactions. Give names of the reactions with one example each. [10]
- (b) Give mechanism of the Norrish type-I process. How many types of carbonyl compounds give this reaction ? Give one example from each compound. [10]

OR

- (a) Give mechanism of Norrish type-II reaction. Explain why cyclopropyl ketones are the most common class of compound for β -cleavage reaction. [10]
- (b) Gas phase irradiation of 2-pentanone produces acetone and ethylene in about 88% yield alongwith 12% 1-methylcyclobutanol. Account for the formation of these three photochemical products. [10]
3. (a) Discuss the chemistry of photo-addition reaction between benzene and alkenes. [10]
- (b) 1,2-dimethylbenzene on irradiation gives a mixture of 1,3 and 1,4-dimethylbenzene via the formation of prismane as reaction intermediate. Give structure of prismanes in both cases. [10]

[3]

OR

- (a) 1,3,5-trimethylbenzene on irradiation with UV gives 1,2,4-trimethylbenzene. This transformation is due to the 1,2-alkyl group shift or 1,3-alkyl group shift. Give mechanism for this transformation. [10]
- (b) Explain why NO_2 is meta directing for photo induced aromatic nucleophilic substitution reactions ? Discuss with example. [10]
4. With example, give mechanism of any two of the following reactions : [10 \times 2]
- (a) Photo-fries rearrangement
- (b) Barton reaction
- (c) Photo degradation of polymer
- (d) Photochemistry of vision