



NATIONAL OPEN UNIVERSITY OF NIGERIA

14/16, Ahmadu Bello Way, Victoria Island

SCHOOL OF SCIENCE AND TECHNOLOGY

October, 2013 Examination

Course Code: CHM 414
hours

TIME:2

Course Title: PHOTOCHEMISTRY AND PERICYCLIC REACTIONS

Answer any four questions

1(a) What are the different types of electromagnetic radiation? What kind of electromagnetic radiation has the shortest wavelength? The longest? (9 marks)

(b) List any three physical processes that take place when radiant energy interacts with an object (3 marks)

(c) A certain source emits radiation of wavelength 500.0 nm. What is the energy, in kJ, of one mole of photons of this radiation? ($h = 6.63 \times 10^{-34} \text{ J s}$; $c = 3 \times 10^8 \text{ m s}^{-1}$; $N_A = 6.02 \times 10^{23} \text{ mole}^{-1}$) (5½ marks)

(d) Give four differences between thermal reactions and photochemical reactions (6 marks)

2(a) What is photochemistry? (3 marks)

(b) State the basic laws of photochemistry (5 marks)

(c) Write equations illustrating any four possible reactions that an electronically excited species may undergo (4 marks)

(d) Give four differences between thermal reactions and photochemical reactions (6 marks)

3(a) With the aid of a simple Jablonski diagram, discuss the fate of a photochemically excited molecule. (7 marks)

(b) (i) State and explain the Franck-Condon principle; (5 marks)

(ii) What is the Stokes' shift? (3 marks)

(c) What do you understand by the term 'photosensitization'? (3 marks)

4(a) (i) What are selection rules in photochemistry? (3 marks)

(ii) Describe the spin selection rule. (3 marks)

(b) Three types of lifetime are known in the field of photochemistry; name and describe them (6 marks)

(c) For naphthalene in a glassy matrix at 77 K excited to the S_1 state, the quantum yield of fluorescence is 0.20, the quantum yield of triplet formation is 0.80, and the quantum yield of phosphorescence is 0.018.

(i) Using the measured lifetime of fluorescence of 96 ns, determine the rate constant for

- intersystem crossing from S_1 to T_1 . (3 marks)
- (ii) From the measured phosphorescence lifetime of 2.6 s, determine the rate constant for intersystem crossing from T_1 to S_0 . (3 marks)
- 5(a)** Define the acronym "LASER" (2 marks)
- (b) Describe briefly the elements of a laser (6 marks)
- (c) Draw and label a diagram that illustrates the four elements of a laser. (4 marks)
- (d) Describe four uses of lasers (6 marks)
- 6(a)** Distinguish between (i) concerted and stepwise processes (ii) synchronous and asynchronous systems. (4 marks)
- (b) Give five characteristics of pericyclic reactions (5 marks)
- (c) What do the following acronyms stand for (i) HOMO (ii) LUMO (iii) SOMO (iv) NBMO (v) FMO? (5 marks)
- (d) State the Woodward-Hoffmann's rule for pericyclic reactions. (3½ marks)