NATIONAL OPEN UNIVERSITY OF NIGERIA
UNIVERSITY VILLAGE, PLOT 91 CADASTRAL ZONE, NNAMDI AZIKIWE EXPRESS WAY, JABI - ABUJA.
FACULTY OF SCIENCES
DEPARTMENT OF CHEMISTRY

2024_2 EXAMINATION

COURSE CODE: **CHM 414**
COURSE TITLE: **PHOTOCHEMISTRY & PERICYCLIC REACTIONS**
COURSE UNIT: **2**
TIME: **2 HOURS**
INSTRUCTION: **ANSWER QUESTION NO. ONE (1) AND ANY OTHER TWO (2) QUESTIONS**

$$\boldsymbol{CONSTANTS: Plank\ constant} = (\mathbf{6.6260 \times 10^{-34}\ m^2 kgs^{-1}})$$
$$\boldsymbol{Speed\ of\ light} = (\mathbf{3 \times 10^{8}\ ms^{-1}})$$
$$\boldsymbol{Avagadros\ number} = \mathbf{6.022 \times 10^{23}\ mol^{-1}}$$

QUESTION ONE

1(a)(i) What are cyclo addition reactions? (2 marks)

(ii) Give the conditions required for a pericyclic reaction to take place based on the Frontier Orbital Theory (2 marks)

(b) Illustrate how thermal electrocyclic ring closure of (2*E*,4*Z*,6*E*)-2,4,6-octatriene could yield a single product with cis-methyl groups on the ring. (5 marks)

(c) Highlight any five (5) differences between photochemical and thermal reactions? In what way is photochemical reaction superior to thermal reaction considering the following: light radiation; light source; temperature; energy of activation? (13 marks)

(d) State any four (4) ways that a molecule can relax prior to fluorescence emission (8 marks)

TOTAL MARK QUESTION 1 = 30 MARKS

QUESTION TWO

2(a)(i) Photolysis of HBr is known to be characterised with two sets of reaction. Name the reaction and write suitable equations for each. Hence write the overall reaction.

(10 marks)

(ii) Write an equation that can be used to calculate the quantum yield of a photochemical reaction. Hence calculate the quantum yield for photolysis of HBr. (4 marks)

(b) Mention any three (3) types of lifetime that exist in photochemistry (3 marks)

(c) Explain briefly the process of photoionization (3 marks)

TOTAL MARK QUESTION 2 = 20 MARKS

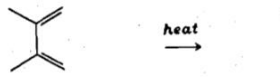
QUESTION THREE

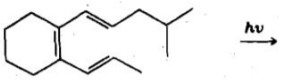
3(a)(i) What is Bioluminescence? (2 marks)

(ii)By the use chemical equation only, distinguish between ionization and isomerization

(2 marks)

(b) Specify which type of rotatory motion (conrotatory or disrotatory) would each of following undergo in an electrocyclisation reaction .

(i) 

(2 marks) (ii) 

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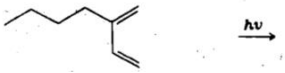
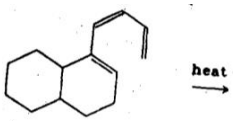
(iii) 

(2 marks) (iv) 

(2 marks)

(c)(i) Distinguish between Antarafacial and suprafacial cycloaddition reactions (4 marks)

(ii) What is the frequency of violet light with a wavelength of 408 nm? (4 marks)

TOTAL MARK QUESTION 3 = 20 MARKS

QUESTION FOUR

4(a)(i) Explain the Laporte selection rule. (4 marks)

(ii)Use chemical equation to illustrate the photochemical reaction involved in photosynthesis? (2 marks)

(b)(i) What is the Franck–Condon factor used to account for? (2 marks)

(ii) Calculate the number of moles of HCl(g) produced by the absorption of one joule of radiant energy of wave length 480 nm in the reaction H_2 (*g*) + Cl_2 (*g*) ⟶ 2HCl (*g*) if the quantum yield of the photochemical radiation is 1.0×10^6 (10 marks)

(c) Highlight the application of photochemistry in photodynamic therapy (2 marks)

TOTAL MARK QUESTION 4 = 20 MARKS

QUESTION FIVE

5(a)(i) Mention any three (3) factors that determine the nature of products formed in pericyclic reactions? (3 marks)

(ii) Give one (1) example of a radioactive relaxation process (1 mark)

(b)(i) Explain why [1,3] Sigmatropic migrations of hydrogen cannot occur under thermal conditions, but [1,3] Sigmatropic migrations of carbon can occur under thermal conditions. (5 marks)

(ii) Discus the Sigmatropic rearrangement in biosynthesis of vitamin D. Use chemical equations to support your answer (9 marks)

(c) What are the HOMO and LUMO in 2,4-hexadiene? (2 marks)

TOTAL MARK QUESTION 5 = 20 MARKS