Photochemistry
Quantum efficiency

Processes of photochemical reactions

The overall photochemical reaction consists of

i) Primary reaction
ii) Secondary reaction

• In the primary reaction, the quantum of light is absorbed by a molecule 'A' formations an excited molecule 'A*'

$$A + h\nu \rightarrow A^*$$

In the secondary reaction, the excited molecules react further to give the product of higher quantum yield.

$$A^* \rightarrow B$$

In terms of Quantum efficiency :

$$\text{Quantum Efficiency } \phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta's of light absorbed at same time}}$$

Experimentally,

$$\phi = \frac{\text{rate of chemical reaction}}{\text{quanta absorbed per second.}}$$

Classification of photochemical reaction based on quantum yield

Three categories

- The reaction in which ϕ is a small integer like 1, 2...

Ex: a) Dissociation of HI & HBr, b) Combination of $SO_2 + Cl_2$ and
c) Ozonisation of O_2

- The reaction in which ϕ <1

Ex: a) Dissociation of NH_3, CH_3COCH_3 & NO_2 and
b) Transformation of maleic acid into fumaric acid.

- The reaction in which ϕ is extremely high

Ex: a) Combination of CO with Cl_2 and b) Combination of H_2 with Cl_2

Reasons for high quantum yield

- ✓Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions
- ✓Formation of intermediate products will act as a catalyst
- ✓If the reactions are exothermic, the heat evolved may activate other molecules
- ✓The active molecules may collide with other molecules and activate them

Reasons for low quantum yield

- ✓ Excited molecules may get deactivated before they form products
- ✓ Excited molecules may lose their energy by collisions with non-excited molecules
- ✓ Molecules may not receive sufficient energy to enable them to react
- ✓ Recombination of dissociated fragments will give low quantum yield.

Dimerization of anthracene to dianthracene

$$2C_{14}H_{10} + h\nu \rightarrow C_{28}H_{20}$$

The quantum yield = 2,
but actually it is found to be = 0.5;

the reason is the above reaction is reversible

$$C_{28}H_{20} \rightarrow 2C_{14}H_{10}$$