

Photochemistry

Quantum efficiency

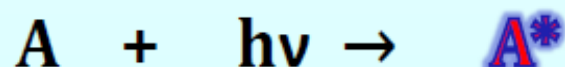


Processes of photochemical reactions

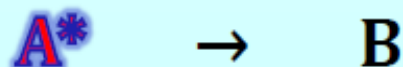
The overall photochemical reaction consists of

- 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*'



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



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,

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



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 $\text{SO}_2 + \text{Cl}_2$ and
c) Ozonisation of O_2

- The reaction in which $\phi < 1$

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



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

the reason is the above reaction is reversible

