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Topic: Primary and Secondary processes with concept of Quantum Yield

UG

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Primary and Secondary reactions

The overall photochemical reaction may consist of :

(*a*) a primary reaction

(*b*) secondary reactions

A primary reaction proceeds by absorption of radiation.

A secondary reaction is a thermal reaction which occurs subsequent to the primary reaction.

For example, the decomposition of HBr occurs as follows :

$HBr + h\nu \longrightarrow H + Br$	Primary reaction
$HBr + H \longrightarrow H_2 + Br$	Secondary reaction
$Br + Br \longrightarrow Br_2$	Secondary reaction
$2HBr + h\nu \longrightarrow H_2 + Br_2$	Overall reaction

Evidently, the primary reaction only obeys the law of photochemical equivalence strictly. The secondary reactions have no concern with the law.

Quantum yield (or Quantum efficiency)

It has been shown that not always a photochemical reaction obeys the Einstein law. The number of molecules reacted or decomposed is often found to be markedly different from the number of quanta or photons of radiation absorbed in a given time.

The number of molecules reacted or formed per photon of light absorbed is termed Quantum yield. It is denoted by φ so that

$$\phi = \frac{\text{No. of molecules reacted or formed}}{\text{No. of photons absorbed}}$$

For a reaction that obeys strictly the Einstein law, one molecule decomposes per photon, the quantum yield $\varphi = 1$. When two or more molecules are decomposed per photon, $\varphi > 1$ and the reaction has a **high quantum yield.** If the number of molecules decomposed is less than one per photon, the reaction has a **low quantum yield.**

Cause of high quantum yield

When one photon decomposes or forms more than one molecule, the quantum yield $\varphi > 1$ and is said to be high. The chief reasons for high quantum yield are :

(*a*) **Reactions subsequent to the Primary reaction.** One photon absorbed in a primary reaction dissociates one molecule of the reactant. But the excited atoms that result may start a subsequent secondary reaction in which a further molecule is decomposed

$$AB + h\nu \longrightarrow A + B \qquad \text{Primary}$$
$$AB + A \longrightarrow A_2 + B \qquad \text{Secondary}$$

Obviously, one photon of radiation has decomposed two molecules, one in the primary reaction and one in the secondary reaction. Hence the quantum yield of the overall reaction is 2.

(*b*) **A reaction chain forms many molecules per photon.** When there are two or more reactants, a molecule of one of them absorbs a photon and dissociates (primary reaction). The excited atom that is produced starts a secondary reaction chain.

$$A_2 + h\nu \longrightarrow 2A \quad ...(1) \quad \text{Primary}$$

$$A + B_2 \longrightarrow AB + B \quad ...(2)$$

$$B + A_2 \longrightarrow AB + A \quad ...(3)$$

(2) and (3): Secondary Reaction chain

It is noteworthy that A consumed in (2) is regenerated in (3). This reaction chain continues to form two molecules each time. Thus the number of AB molecules formed in the overall reaction per photon is very large. Or that the quantum yield is extremely high.

Examples of high quantum yield

The above reasons of high quantum yield are illustrated by citing examples as below:

(*i*) **Decomposition of HI.** The decomposition of hydrogen iodide is brought about by the absorption of light of less than 4000 A. In the primary reaction, a molecule of hydrogen iodide absorbs a photon and dissociates to produce H and I. This is followed by secondary steps as shown below :

$$HI + h\nu \longrightarrow H + I \quad ...(1) \quad \text{Primary}$$

$$H + HI \longrightarrow H_2 + I \quad ...(2)$$

$$I + I \longrightarrow I_2 \quad ...(3)$$

Secondary

$$2HI + h\nu \longrightarrow H_2 + I_2 \quad \text{Overall reaction}$$

In the overall reaction, two molecules of hydrogen iodide are decomposed for one photon (hv)

of light absorbed. Thus the quantum yield is 2.

(*ii*) **Hydrogen-Chlorine reaction**. This is a well known example of a **photochemical chain reaction.** A mixture of hydrogen and chlorine is exposed to light of wavelength less than 4000 A. The hydrogen and chlorine react rapidly to form hydrogen chloride. In the primary step, a molecule of chlorine absorbs a photon and dissociates into two Cl atoms. This is followed by the secondary reactions stated below :

$$Cl_2 + hv \longrightarrow 2Cl \quad ...(1) \quad \text{Primary reaction}$$

$$Cl + H_2 \longrightarrow HCl + H \quad ...(2)$$
$$H + Cl_2 \longrightarrow HCl + Cl \quad ...(3)$$
Secondary reactions

The Cl atom used in step (2) is regenerated in step (3). Thus the steps (2) and (3) constitute a self-propagating chain reaction. This produces two molecules of HCl in each cycle. Thus one photon of light absorbed in step (1) forms a large number of HCl molecules by repetition of the reaction sequence (2) and (3). The chain reaction terminates when the Cl atoms recombine at the walls of the vessel where they lose their excess energy.

$$2Cl \xrightarrow{\text{walls}} Cl_2$$

The number of HCl molecules formed for a photon of light is very high. The quantum yield of the reaction varies from 10^4 to 10^6.

Causes of low quantum yield

The chief reasons of low quantum yield are :

(*a*) **Deactivation of reacting molecules.** The excited molecules in the primary process may be deactivated before they get opportunity to react. This is caused by collisions with some inert molecules or by fluorescence.

$$A + h\nu \longrightarrow A^* \qquad \textit{Activation}$$
$$A^* \longrightarrow A + h\nu' \qquad \textit{Fluorescence}$$

(*b*) **Occurrence of reverse of primary reaction.** Here the primary reaction generally yields a polymer. The product then undergoes a thermal reaction giving back the reactant molecules.

$$2A \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} A_2$$

The reverse thermal reaction proceeds till the equilibrium state is reached.

(*c*) **Recombination of dissociated fragments.** In a primary process the reactant molecules may dissociate to give smaller fragments. These fragments can recombine to give back the reactant.

$$(AB) + h\nu \longrightarrow A + B$$

$$A + B \longrightarrow (AB)$$

Thus the secondary reactions involving the fragments to form the product will not occur. This will greatly lower the yield.

The yield of particular photochemical reaction may be lower than expected for more than one reason cited above.

Examples of low quantum yield

The examples listed below will illustrate the above causes of low quantum yield:

(*i*) **Dimerization of Anthracene.** When anthracene, $C_{14}H_{10}$, dissolved in benzene is exposed to ultraviolet light, it is converted to dianthracene, $C_{28}H_{20}$.

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

Obviously, the quantum yield should be 2 but it is actually found to be 0.5. The low quantum yield is explained as the reaction is accompanied by fluorescence which deactivates the excited anthracene molecules. Furthermore, the above reaction is reversible.

$$2C_{14}H_{10} \underset{\text{thermal}}{\overset{h\nu}{\rightleftharpoons}} C_{28}H_{20}$$

The transformation of the product back to the reactant occurs till a state of equilibrium is reached. This further lowers the quantum yield.

(*ii*) **Combination of H_2 and Br_2.** When a mixture of hydrogen and bromine is exposed to light, hydrogen bromide is formed. The reaction occurs by the following possible steps.

$$Br_2 + hy \longrightarrow 2Br \quad ...(1) \quad \text{Primary reaction}$$

$$\left.\begin{array}{lll} Br + H_2 \longrightarrow HBr + H & & ...(2) \\ H + Br_2 \longrightarrow HBr + Br & & ...(3) \\ H + HBr \longrightarrow H_2 + Br & & ...(4) \\ Br + Br \longrightarrow Br & & ...(5) \end{array}\right\} \text{Secondary reactions}$$

The reaction (2) is extremely slow. The reactions (3), (4) and (5), depend directly or indirectly on (2) and so are very slow. Therefore most of the Br atoms produced in the primary process recombine to give back Br_2 molecules. Thus the HBr molecules obtained per quantum is extremely small. The quantum yield of the reaction is found to be 0.01 at ordinary temperature.

CALCULATION OF QUANTUM YIELD

By definition, the quantum yield, p, of a photochemical reaction is expressed as :

$$¢ = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of photons of radiation energy absorbed}}$$

or

$$¢ = \frac{\text{Number of moles decomposed or formed}}{\text{Number of moles of radiation energy absorbed}}$$

Thus we can calculate quantum yield from :

(*a*) The amount of the reactant decomposed in a given time and

(*b*) The amount of radiation energy absorbed in the same time

The radiation energy is absorbed by a chemical system as photons. Therefore we should know the energy associated with a photon or a mole of photons.