$$E = \frac{2.859}{\lambda} \times 10^5 \text{ kcal mol}^{-1}$$

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 :

$$HBr + h\nu \longrightarrow H + Br \quad \text{Primary reaction}$$
$$HBr + H \longrightarrow H_2 + Br \quad \text{Secondary reaction}$$
$$Br + Br \longrightarrow Br_2 \quad \text{Secondary reaction}$$

$$2HBr + h\nu \longrightarrow H_2 + Br_2 \quad \text{Overall reaction}$$

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 $\phi = 1$. When two or more molecules are decomposed per photon, $\phi > 1$ 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 $\phi > 1$ 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

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

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.

$$A_2 + h\nu \longrightarrow 2A \quad ...(1) \quad \text{Primary}$$
$$\left.\begin{aligned} A + B_2 &\longrightarrow AB + B \quad ...(2) \\ B + A_2 &\longrightarrow AB + A \quad ...(3) \end{aligned}\right\} \text{Secondary Reaction chain}$$

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 Å. 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 :

$$HI + h\nu \longrightarrow H + I \quad ...(1) \quad \text{Primary}$$
$$H + HI \longrightarrow H_2 + I \quad ...(2)$$
$$I + I \longrightarrow I_2 \quad ...(3) \quad \Big\} \text{Secondary}$$
$$2HI + h\nu \longrightarrow H_2 + I_2 \quad \text{Overall reaction}$$

In the overall reaction, two molecules of hydrogen iodide are decomposed for one photon ($h\nu$) 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 Å. 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 :

$$Cl_2 + h\nu \longrightarrow 2Cl \quad ...(1) \quad \text{Primary reaction}$$
$$Cl + H_2 \longrightarrow HCl + H \quad ...(2)$$
$$H + Cl_2 \longrightarrow HCl + Cl \quad ...(3) \quad \Big\} \text{Secondary reactions}$$

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.

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

(*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.

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

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.

$$Br_2 + h\nu \longrightarrow 2Br \quad ...(1) \quad \text{Primary reaction}$$
$$Br + H_2 \longrightarrow HBr + H \quad ...(2)$$
$$\left.\begin{aligned} H + Br_2 &\longrightarrow HBr + Br \quad ...(3)\\ H + HBr &\longrightarrow H_2 + Br \quad ...(4)\\ Br + Br &\longrightarrow Br \quad ...(5)\end{aligned}\right\} \text{Secondary reactions}$$

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, ϕ, of a photochemical reaction is expressed as :

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

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

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.

The energy of photons; einstein

We know that the energy of a photon (or quantum), $\in$, is given by the equation.

$$\in = h\nu = \frac{hc}{\lambda} \qquad ...(1)$$

where h = Planck's constant (6.624×10^{-27} erg-sec)
ν = frequency of radiation
λ = wavelength of radiation
c = velocity of light (3×10^{10} cm sec^{-1})

If λ is given in cm, the energy is expressed in ergs.

The energy, *E*, of an Avogadro number (*N*) of photons is referred to as one einstein. That is,

$$E = \frac{Nhc}{\lambda} \qquad ...(2)$$

Substituting the values of N (= 6.02×10^{23}), h and c, in (2), we have

$$E = \frac{1.196 \times 10^8}{\lambda} \text{ erg mol}^{-1}$$

If λ is expressed in Å units (1Å = 10^{-8} cm),

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1} \qquad ...(3)$$

Since 1 cal = 4.184×10^7 erg, energy in calories would be

$$E = \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^7} \qquad ...(4)$$

$$= \frac{2.859}{\lambda} \times 10^8 \text{ cal mol}^{-1}$$

or
$$E = \frac{2.859}{\lambda} \times 10^5 \quad \text{kcal mol}^{-1} \qquad ...(5)$$

It is evident from (3) that the numerical value of einstein varies inversely as the wavelength of radiation. **The higher the wavelength, the smaller will be the energy per einstein.**

SOLVED PROBLEM 1. Calculate the energy associated with (*a*) one photon; (*b*) one einstein of radiation of wavelength 8000 Å. $h = 6.62 \times 10^{-27}$ erg-sec; $c = 3 \times 10^{10}$ cm sec^{-1}.

SOLUTION

(*a*) Energy of a photon

$$= \frac{hc}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{8000 \times 10^{-8}}$$

$$= \frac{6.62 \times 3}{8.0} \times 10^{-12} \text{ erg} = 2.4825 \times 10^{-12} \text{ erg}$$

(*b*) Energy per einstein

$$= \frac{Nhc}{\lambda} = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}{8000 \times 10^{-8}}$$

$$= \frac{6.02 \times 6.62 \times 3}{8.0} \times 10^{11} \text{ erg} = \mathbf{1.4945 \times 10^{12}} \textbf{ erg}$$

SOLVED PROBLEM 2. When a substance *A* was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. In the same time *A* absorbed 2.0×10^6 photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION

Number of molecules of A reacting = $0.002 \times N = 0.002 \times 6.02 \times 10^{23}$

Number of photons absorbed per second = 2.0×10^6

Number of photons absorbed in 20 minutes and 4 seconds = $2.0 \times 10^6 \times 1204$

Quantum yield $$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

$$= \frac{0.002 \times 6.02 \times 10^{23}}{2.0 \times 10^6 \times 1204} = \mathbf{5.00 \times 10^{11}}$$

SOLVED PROBLEM 3. When irradiated with light of 5000 Å wavelength, 1×10^{-4} mole of a substance is decomposed. How many photons are absorbed during the reaction if its quantum efficiency is 10.00. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION

Quantum efficiency of the reaction = 10.00

No. of moles decomposed $= 1 \times 10^{-4}$

No. of molecules decomposed $= 1 \times 10^{-4} \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{19}$

we know that,

$$\phi = \frac{\text{No. of molecules decomposed}}{\text{No. of photons absorbed}}$$

$$= \frac{6.02 \times 10^{19}}{\text{No. of photons absorbed}}$$

No. of photons absorbed $$= \frac{6.02 \times 10^{19}}{10} = \mathbf{6.02 \times 10^{18}}$$

SOLVED PROBLEM 4. When propionaldehyde is irradiated with light of λ = 3020 Å, it is decomposed to form carbon monoxide.

$$CH_3CH_2CHO + h\nu \longrightarrow CH_3CH_3 + CO$$

The quantum yield for the reaction is 0.54. The light energy absorbed is 15000 erg mol in a given time. Find the amount of carbon monoxide formed in moles in the same time.

SOLUTION

From expression (3), we have

$$\text{one einstein } (E) = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}$$

$$\text{when } \lambda = 3020 \text{ Å, one einstein} = \frac{1.196 \times 10^{16}}{3020} \text{ erg mol}$$

$$\text{or} \quad 15000 \text{ erg mol of energy} = \frac{15000 \times 3020}{1.196 \times 10^{16}} = 3.78 \times 10^{-9} \text{ einstein}$$

But $$\phi = \frac{\text{No. of moles of CO formed}}{\text{No. of einsteins absorbed}} = 0.54$$

Hence the amount of CO formed = $0.54 \times 3.78 \times 10^{-9}$ = $\mathbf{2.04 \times 10^{-9}}$ **moles**

PHOTOSENSITIZED REACTIONS

In many photochemical reactions the reactant molecule does not absorb the radiation required for the reaction. Hence the reaction is not possible. In such cases the reaction may still occur if a foreign species such as mercury vapour is present. The mercury atom absorbs the incident radiation and subsequently transfers its energy to the reactant molecule which is activated. Thus the reaction occurs. A species which can both absorb and transfer radiant energy for activation of the reactant molecule, is called a **photosensitizer.** The reaction so caused is called a **photosensitized reaction.**

The role of mercury vapour is that of a go-between. The mercury atom absorbs the incident radiation and is excited. The excited atom collides with a reactant molecule (A) and transfer to it the excitation energy. This energy is enough to activate the molecule (A). The mercury atom returns to the original unactivated state.

$$\text{Hg} + h\nu \longrightarrow \text{Hg}^*$$
$$\text{Hg}^* + \text{A} \longrightarrow \text{A}^* + \text{Hg}$$

Examples of Photosensitized reactions

(*a*) **Reaction between H_2 and O_2.** This reaction is photosensitized by mercury vapour. The product is hydrogen peroxide, H_2O_2.

$$\text{Hg} + h\nu \longrightarrow \text{Hg}^* \qquad \text{Primary absorption}$$
$$\text{Hg} + \text{H}_2 \longrightarrow 2\text{H} + \text{Hg} \qquad \text{Energy transfer}$$
$$\left.\begin{array}{l}\text{H} + \text{O}_2 \longrightarrow \text{HO}_2 \\ \text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2\end{array}\right\} \text{Reaction}$$

Hydrogen peroxide may decompose to form water, H_2O.

(*b*) **Reaction between H_2 and CO.** Mercury vapour is used as photosensitizer. The product is formaldehyde, HCHO.

$$\text{Hg} + h\nu \longrightarrow \text{Hg}^* \qquad \text{Primary absorption}$$
$$\text{Hg} + \text{H}_2 \longrightarrow 2\text{H} + \text{Hg} \qquad \text{Energy transfer}$$
$$\text{H} + \text{CO} \longrightarrow \text{HCO}$$
$$\left.\begin{array}{l}\text{HCO} + \text{H}_2 \longrightarrow \text{HCHO} + \text{H} \\ 2\text{HCO} \longrightarrow \text{HCHO} + \text{CO}\end{array}\right\} \text{Reaction}$$

Some glyoxal, CHO-CHO, is also formed by dimerization of formyl radicals, HCO.

PHOTOPHYSICAL PROCESSES

If the absorbed radiation is not used to cause a chemical change, it is re-emitted as light of longer wavelength. The three such photophysical processes which can occur are :

(*a*) Fluorescence (*b*) Phosphorescence (*c*) Chemiluminescence

Fluorescence

Certain molecules (or atoms) when exposed to light radiation of short wavelength (high frequency), emit light of longer wavelength. The process is called **fluorescence** and the substance that exhibits fluorescence is called florescent substance. Florescence stops as soon as the incident radiation is cut off.

Examples. (*a*) a solution of quinine sulphate on exposure to visible light, exhibits blue fluorescence.

(*b*) a solution of chlorophyll in ether shows blood red fluorescence.