reaction

4.13. PHOTOCHEMICAL EQUILIBRIUM OR PHOTOSTATIONARY STATE

Suppose a substance *A* changes into a substance *B* by the absorption of light *i.e.*, the reaction $A \rightarrow B$ is a photochemical reaction. If the reverse reaction can also occur either as a *photochemical reaction* or as *thermal reaction (dark reaction)*, the situation may be represented as

$$A \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} B \quad \text{or} \quad A \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} B$$

In either case, a stage may reach when the rate of forward reaction may become equal to the rate of backward reaction. Now the absorption of light produces no further chemical change. The reaction is then said to have attained a '*photochemical equilibrium*' or a '*photostationary state*'

Examples : (*i*) *Photochemical decomposition of nitrogen dioxide*

$$2NO_2 \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} 2NO + O_2$$

(*ii*) *Dimerization of anthracene :*

$$2C_{14}H_{10} \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} C_{28}H_{20}$$

(*iii*) *Photochemical decomposition of sulphur trioxide*

$$2SO_3 \underset{\text{Light}}{\overset{\text{Light}}{\rightleftharpoons}} 2SO_2 + O_2$$

Equilibrium constant : The equilirbium constant of a photochemical equilibrium is different from that of the ordinary chemical equilibrium. This is obviously due to the fact that the rate of a photochemical reaction does not depend upon the concentration of the reactants but it depends upon the intensity of the light absorbed. Thus for the reaction

$$A \underset{\text{Thermal}}{\overset{\text{Light}}{\rightleftharpoons}} B$$

Rate of forward reaction $\propto I_{abs} = k_1 I_{abs}$

Rate of backward reaction $\propto [B] = k_2\,[B]$

When the reaction is in equilibrium, Rate of forward reaction = Rate of backward reaction

$$\text{i.e.}\quad k_1 I_{abs} = k_2\,[B] \quad \text{or} \quad \frac{k_2}{k_1} = \frac{I_{abs}}{[B]} \quad \text{or} \quad K = \frac{I_{abs}}{[B]}$$

where $K = \frac{k_2}{k_1}$ is the **photochemical equilibrium constant.**

From the above equation, it is the clear that photochemical equilibrium constant depends upon the intensity of the light absorbed.

Further, the above equation may be written as $[B] = \frac{k_1}{k_2} I_{abs}$

It follows that the concentration of the products formed at equilibrium is directly proportional to the intensity of the light absorbed.

or

$$\boxed{\frac{\phi_0}{\phi_Q} = 1 + k_{SV}\,[Q]} \quad ...(5)$$

This equation is known as **Stern-Volmer** equation and the constant k_{SV} is called Stern-Volmer constant. This equation shows that ϕ_0/ϕ_Q varies linearly with [Q]. The slope of the line will be k_{SV}, *i.e.* $k_3\tau$ from which value of τ can be obtained. ...(6)

4.11. PHOTOSENSITIZATION

There are many substances which do not react directly when exposed to light. However, if another substance is added, the photochemical reaction starts. The substance thus added itself does not undergo any chemical change. It merely absorbs the light energy and then passes it on to one of the reactants. *Such a substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not under go any chemical change is called a photosensitizer and the process is called photosensitization.* Thus a photosensitizer simply acts as a *carrier of energy*.

At the first instance it appears that a photosensitizer is similar to a catalyst. However, this is not so as they act by different mechanism.

Examples of Photosensitized Reactions. A few well known examples of the photosensitized reactions are briefly described below :

1. *Dissociation of hydrogen molecules in presence of mercury vapour.* Hydrogen molecules do no dissociate when exposed to ultraviolet light (of 2537 Å emitted by the mercury vapour lamp). Howeve when hydrogen gas is mixed with mercury vapour and then exposed to ultraviolet light, hydrogen molecule dissociate to give hydrogen atoms through the following reactions :

$$Hg + h\nu \longrightarrow Hg^*$$

$$Hg^* + H_2 \longrightarrow Hg + 2H$$

where Hg* represents the activated mercury atom. Thus in the above reaction, mercury acts a photosensitizer.

The H-atom being highly reactive can easily reduce metallic oxides, nitrous oxide, carbon monoxide etc.

In a similar manner, the dissociation of NH_3, PH_3 AsH_3 and a number of organic compounds is photosensitized by mercury. Certain combination reactions *e.g.*,

$2H_2 + O_2 \longrightarrow 2H_2O\,;\ N_2 + 3H_2 \longrightarrow 2NH_3;\ 3O_2 \longrightarrow 2O_3$ etc. are also mercury-photosensitized.

Two well known mercury photosensitized reactions involving dissociation of H_2 molecules into H atoms are briefly explained below :

(*a*) *Combination between CO and H_2 to form formaldehyde and glyoxal.* It is believed to take place through the following steps :

(*i*) $Hg + h\nu \longrightarrow Hg^*$ (Activation)

(*ii*) $Hg^* + H_2 \longrightarrow 2H + Hg$ (Dissociation)

(*iii*) $H + CO \longrightarrow HCO$

(*iv*) $HCO + H_2 \longrightarrow HCHO + H$

(*v*) $2HCO \longrightarrow HCHO + CO$

(*vi*) $2HCO \longrightarrow OHC{-}CHO$ (Glyoxal)

(*b*) *Combination between H_2 and O_2 to form H_2O and H_2O_2.* It is believed to take place through the following steps :

(*i*) $Hg + h\nu \longrightarrow Hg^*$ (Activation)

(*ii*) $Hg^* + H_2 \longrightarrow 2H + Hg$ (Dissociation)

(*iii*) $H + O_2 \longrightarrow HO_2$

(*iv*) $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$

(*v*) $HO_2 + H_2 \longrightarrow H_2O_2 + H$ (resulting into a chain reaction)

H_2O_2 may be isolated as such or it decomposes to give H_2O and O_2. However, under certain conditions, the amount of H_2O_2 predominates. Cadmium vapours have also been used as photosensitizer in a number of reactions such as polymerization of ethylene, decomposition of ethane, propane etc. into H_2 and lower hydrocarbons etc.

2. *Decomposition of ozone in presence of chlorine as photosensitizer.* Ultraviolet radiations are absorbed by Cl_2 molecules and dissociate them into Cl atoms but they have very little effect on the decomposition of ozone. However, if the mixture of ozone and chlorine is exposed to these radiations, ozone is readily decomposed whereas chlorine remains almost unchanged at the end of the reaction. Chlorine then acts as a photosensitizer in the decomposition of ozone. The reaction starts by absorption of radiation of wavelength 4785 Å by Cl_2 molecules resulting into its dissociation into Cl atoms followed by other reactions. Thus we have

(*i*) $Cl_2 + h\nu \longrightarrow 2Cl$

(*ii*) $Cl + O_3 + X \longrightarrow ClO_3^{\bullet} + X$

(*iii*) $ClO_3^{\bullet} + O_3 \longrightarrow ClO_2 + 2O_2$

(*iv*) $ClO_2 + O_3 \longrightarrow ClO_3 + O_2$

where X is any molecule capable of absorbing energy and then transferring it to the reactants.

The above mechanism is supported by the fact that presence of the acids, $HClO_3$ and $HClO_4$, has been detected if moisture is present. Further, polymer Cl_2O_6 has also been isolated and identified which is formed from the excited $ClO_3^{\bullet}$ radicals. These radicals also partly decompose to give Cl_2 and O_2.

A few more examples of chlorine-photosensitized reactions are given below :

(*i*) $2SO_2 + O_2 \xrightarrow[h\nu]{Cl_2} 2SO_3$

(*ii*) $2H_2 + O_2 \xrightarrow[h\nu]{Cl_2} 2H_2O$

(*iii*) $2PH_3 \xrightarrow[h\nu]{Cl_2} 2P + 3H_2$

3. *Decomposition of Diazomethane (CH_2N_2) is presence of Benzophenone as photosenistizer.* The reaction is believed to take place in presence of radiation of wavelength 3200 Å as follows :

$$Bz \xrightarrow{h\nu} Bz^*$$

$$Bz^* + CH_2N_2 \longrightarrow Bz + CH_2N_2^{\bullet}$$

$$CH_2N_2^{\bullet} \longrightarrow \underset{\text{Methylene}}{CH_2} + N_2$$

4. *Isomerization of But-2-ene from cis to trans in presence of SO_2 as photosensitizer.* The reaction takes place when exposed to radiation of wavelength 2573 Å as follows :

$$SO_2 \xrightarrow{h\nu} SO_2^{\bullet}$$

$$SO_2^{\bullet} + \text{cis-But-2-ene} \longrightarrow SO_2 + \text{cis-But-2-ene}^*$$

$$\text{cis-But-2-ene}^* \longrightarrow \text{trans-But-2-ene}^*$$

$$\downarrow$$

$$\text{trans-But-2-ene}$$

5. *Decomposition of oxalic acid in presence of uranyl sulphate.* This is an example of a photosensitized reaction taking place in solution (liquid phase). As already discussed, this reaction forms the basis of the actinometer used to measure the intensity of radiation. The coloured uranyl ions absorb the light and then pass it on to the colourless oxalic acid which then undergoes decomposition ; the extent of decomposition depending upon the light energy absorbed.

$$UO_2^{2+} + h\nu \longrightarrow UO_2^{2+\bullet}$$

$$UO_2^{2+\bullet} + \begin{array}{c} COOH \\ | \\ COOH \end{array} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The uranyl ions thus act as photosensitizer and are used over and again.

It is important to add here that in the absence of uranyl compound, the quantum yield is very low (<0.01). For sensitized reaction, it is ≥ 0.5. It may further be mentioned here that the exact mechanism by which UO_2^{2+} – sensitized dissociation of oxalic acid occurs is not certain. It is believed that most probably a complex is fomed between the acid and UO_2^{2+} ions.

6. *Photosynthesis of carbohydrates in plants.* This is a process occurring in plants every day during the sunlight. Carbon dioxide and water vapour present in the air do not absorb the visible light (emitted by the sun). However, the green colouring matter, namely *chlorophyll* present in the plants can absorb the visible light. After absorption, it passes on the energy to the carbon dioxide and water molecules which then combine to form carbohydrates alongwith the evolution of oxygen.

$$\underbrace{CO_2 + H_2O}_{\text{From air}} + \underset{\substack{\text{From}\\\text{sunlight}}}{h\nu} \xrightarrow{\text{Chlorophyll}} \underset{\text{Glucose}}{\frac{1}{6}(C_6H_{12}O_6)} + O_2$$

Thus chlorophyll acts as a photosensitizer in the above reaction.