

# PHOTOCHEMISTRY

B.sc – III(HONS)

20-11-2021

AUTHOR – GYAN PRAKASH

DR. SHASHI KUMAR

HOD DEPARTMENT OF CHEMISTRY G.J COLLEGE  
RAMBAG BIHTA (PATNA)

## PHOTOCHEMISTRY:-

### The law of photochemistry:-

There are two laws of photochemistry other than Lambert – Beer law.

#### (1) The Grotthuss - Draper law:-

This law given by Grotthuss and Draper. According to this law all the light that is incident on a sample is not effective in bringing about a chemical change, but only that light which is absorbed by a system can bring about a photochemical reaction.

This law is also called as principle of photochemical activation.

#### (2) The Stark – Einstein law of photochemical equivalent:-

This law was given by Stark (1908) and Einstein (1912).

“According to this law, one molecule is activated by the absorption of one quantum of radiation in the first step of a photochemical reaction”.

However, this law does not mean that a molecule must react after absorption of a photon.

This law is also called as principle of quantum activation.

$$\phi \longrightarrow \text{Fi}$$
$$C = \nu\lambda$$

Thus, according to this law-

$$E = N_A h \nu = N_A h \frac{C}{\lambda}$$

Here, E = Total energy absorbed by one mole of the reacting substance.

$N_A$  = Avogadro's number.

$h$  = Planck's constant.

$\nu$  = Frequency of radiation.

Hence,  $E \propto \frac{1}{\lambda}$

Thus, smaller the wavelength of radiation large will be the energy and vice versa.

The quantity  $E$ , the energy absorbed per mole of the reacting substance is called as one Einstein.

Quantum efficiency or quantum yield ( $\phi$ ):-

$$\begin{aligned}\phi &= \frac{\text{Number of molecules that react}}{\text{Number of quanta of radiation absorbed}} \\ &= \frac{\text{Number of moles that react}}{\text{Number of Einsteins of radiation absorbed}}\end{aligned}$$

The quantum yield of product formation is similarly defined as-

$$\begin{aligned}\phi &= \frac{\text{Number of molecules of product formed}}{\text{Number of quanta of radiation absorbed}} \\ &= \frac{\text{Number of moles of product formed}}{\text{Number of Einsteins of radiation absorbed}}\end{aligned}$$

Number of Einstein of radiation absorbed.

If the law is correct the quantum yield should be unity. This, however is very rare. The quantum yield may be several photochemical reactions. The reasons for this, divergences would be discussed shortly.

The quantum yields of some important photochemical reactions are given below-

Reaction	Quantum yield ( $\phi$ )
$2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$	0.2

$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$	2
$2\text{HBr} \longrightarrow \text{H}_2 + \text{Br}_2$	2
$\text{H}_2 + \text{Cl} \longrightarrow 2\text{HCl}$	$10^4 - 10^6$
$\text{Co} + \text{Cl} \longrightarrow \text{CoCl}_2$	$10^3$
$\text{SO}_2 + \text{Cl}_2 \longrightarrow \text{SO}_2\text{Cl}_2$	1
$2\text{NO}_2 \longrightarrow 2\text{NO} + \text{O}_2$	0.7
$\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$	0.01
$\text{H}_2\text{S} \longrightarrow \text{H}_2 + \text{S}$	1
$3 \text{O}_2 \longrightarrow 2 \text{O}_3$	3

It is evident from above examples that the law of photochemical equivalence strictly valid for a very few reactions only.

The various photochemical reactions can be divided into three categories.

- (i) Those in which the quantum yield is a small integer such as 1, 2, 3... etc.
  - (ii) Those in which quantum yield is less than.
  - (iii) Those in which quantum yield is extremely high.
- (A) In order to explain the above variations Bodenstein pointed.

(1) Primary process:-

According to this process a quantum of light  $h\nu$  is absorbed by a molecule "A" resulting in the formation of an excited molecule  $A^*$ .

Thus,



The molecule which absorbed light may get dissociated yielding atoms or radicals.

(2) Secondary process :-

According to this process the excited atoms, molecules or free radicals produced in the primary process react further giving rise to higher quantum yields.

Sometimes, the atoms or free radicals initiate a series of chain reactions as for example, in the combination of  $\text{H}_2$  and  $\text{Cl}_2$  to give  $\text{HCl}$ , the quantum yields are of the order of  $10^6$  or more.

If the secondary reaction is exothermic the heat of the reaction may activate other molecules there, by causing them to react. This is another reason for higher quantum yield.

The reasons for low quantum yields are-

- (a) Excited molecules may get deactivated before they form products.
- (b) Collisions of excited molecules with non – excited molecules may cause the former to lose their energy.
- (c) The primary photochemical process may get reversed.
- (d) The dissociated fragments may recombine to form the original molecule.

Bodenstein and others emphasised that the law of photochemical equivalence can be applied only to primary process in which each molecule capable of entering into chemical reaction absorbs one quantum of radiation. The

secondary process take place of themselves quite independent of the light radiation.

(B) Discuss photochemical reaction between hydrogen and bromine.

The photochemical combination between hydrogen and bromine to form hydrogen bromide is an example of a chain reaction. Its mechanism is similar to the thermal reaction with the difference that the initiation reaction is brought about by the absorption of a photon by a bromine molecule.

Chain initiation :-

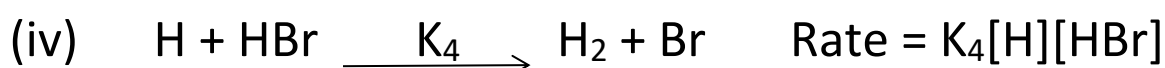


The rest part of the mechanism is similar to the thermal reaction.

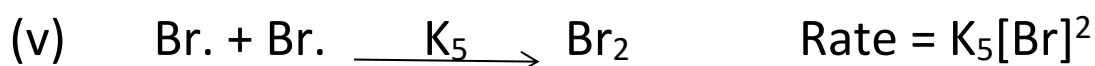
Chain propagation:-



Chain emhibition :-



Chain breaking :-



Here,  $K_1$ ,  $K_2$ ,  $K_3$ ,  $K_4$  and  $K_5$  represent the specific rates of all the five reactions respectively.

Derivation of rate law :-

Since HBr is produced in (ii) and (iii) and removed by the reaction (iv) the net rate of formation of HBr is given by.

$$\frac{d[\text{HBr}]}{dt} = K_2[\text{Br}][\text{H}_2] + K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}] \longrightarrow (1)$$

As equation involves concentration of hydrogen and bromine atoms which are too small quantities to be measured directly, it is required that their concentration must be expressed in measurable quantities. This is done by writing down and solving steady – state equation for [H] and [Br].

Now, Br – atoms are formed by (i), (iii) and (iv) and are removed by (ii) and (v). So, the net rate of formation of Br is given by –

$$\frac{d[\text{Br}]}{dt} = K_1 \text{ Iabs} + K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}] - K_2[\text{Br}][\text{H}_2] - K_5[\text{Br}]^2 \longrightarrow (2)$$

Again H – atoms are formed by reaction (ii) and removed by reaction (iii) and (iv) then,

$$\frac{d[\text{H}]}{dt} = K_2[\text{Br}][\text{H}_2] - K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}] \longrightarrow (3)$$

When the stationary state is reached it follows that –

$$\frac{d[\text{H}]}{dt} = 0 \quad \text{and} \quad \frac{d[\text{Br}]}{dt} = 0$$

Therefore equation (2) and (3) becomes as –

$$K_1 \text{ Iabs} + K_3[\text{H}][\text{Br}_2] + K_4[\text{H}][\text{HBr}] - K_2[\text{H}][\text{Br}] - K_5[\text{Br}]^2 = 0 \longrightarrow (4)$$

$$K_2[\text{Br}][\text{H}_2] - K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}] = 0 \longrightarrow (5)$$

Now, by adding equation (4) and (5) we have –

$$K_1 \text{ Iabs} - K_5[\text{Br}]^2 = 0$$

$$\text{Or, } [\text{Br}] = \sqrt{\frac{K_1}{K_5}} \text{ Iabs} \longrightarrow (6)$$

Now, after putting the value of [Br] from equation (6) to (5) we have –

$$K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs - K_3[H][Br_2] - K_4[H][HBr] = 0$$

$$\text{Or, } K_3[H][Br_2] + K_4[H][HBr] = K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs$$

$$\text{Or, } [H][K_3\{Br_2\} + K_4\{HBr\}] = K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs$$

$$\therefore [H] = x = \frac{K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs}{K_3[Br_2] + K_4[HBr]} \longrightarrow (7)$$

Now, after putting the value of [H] and [Br] from equation (7) and (6) in equation (1) we have –

$$\frac{d[HBr]}{dt} = K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs + \frac{K_3[Br_2] K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs}{K_3[Br_2] + K_4[HBr]} -$$

$$\frac{K_4[HBr] K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs}{K_3[Br_2] + K_4[HBr]}$$

$$\text{or, } \frac{d[HBr]}{dt} = K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs \left[ 1 + \frac{K_3[Br_2]}{K_3[Br_2] + K_4[HBr]} - \frac{K_4[HBr]}{K_3[Br_2] + K_4[HBr]} \right]$$

$$\text{or, } \frac{d[HBr]}{dt} = \frac{K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs}{K_3[Br_2] + K_4[HBr]} \left[ K_3[Br_2] + K_4[HBr] + K_3[Br_2] - K_4[HBr] \right]$$

$$\text{or, } \frac{d[HBr]}{dt} = \frac{2 K_3[Br_2] K_2[H_2] \sqrt{\frac{K_1}{K_5}} Iabs}{K_3[Br_2] + K_4[HBr]} \longrightarrow (8)$$

Now, after dividing the numerator and denominator of equation (8) by  $K_3[Br_2]$  we have –



$$\frac{d[\text{HBr}]}{dt} = \frac{2 K_2 [\text{H}_2] \sqrt{\frac{K_1}{K_5}} I_{abs}}{1 + \frac{K_4}{K_3} \frac{[\text{HBr}]}{[\text{Br}_2]}} = \frac{K' [\text{H}_2] \sqrt{\frac{K_1}{K_5}} I_{abs}}{1 + \frac{[\text{HBr}]}{m' [\text{Br}_2]}} \quad (9)$$

Here,  $K' = 2k_2$  and  $m' = \frac{K_4}{K_3}$  are two constants.

Bodenstein also found equation (9) with the help of experiment.

In spite of the chain mechanism similar to hydrogen and chlorine reaction the quantum yield of this photochemical reaction is very low, being about 0.01 at ordinary temperature. This is due to following reasons –

- (a) Reaction (2) is highly endothermic and therefore, takes place. So, slowly at ordinary temperatures that most of the Bromine atoms recombine to form Bromine molecules. Therefore, the reactions (3), (4) and (5) which are due to reaction (2) cannot occur. Hence, the quantum yield is extremely small.
- (b) With increasing time, the reversal reaction becomes predominate and hence the rate of formation of HBr decreases.

### Photochemical reaction of Hydrogen and Chlorine:-



The special fact about this reaction are –

- (1) The reaction is provoked by the light absorption of chlorine in the region of  $4785\text{\AA}$ .
- (2) The induction period is often absorbed. This is a period after the start of illumination during which the reaction is either very slow or not to take place at all.

The induction period is due to the presence of impurities like  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{O}_2$  etc. that is why with pure  $\text{H}_2$  and  $\text{Cl}_2$  no induction period is observed.

(3) It has been found that the rate of reaction is inversely proportional to the concentration of oxygen.

(4) The quantum yield varies from  $10^4$  to  $10^6$  in the absence of  $\text{O}_2$  and impurities.

Reaction of  $\text{H}_2$  and  $\text{Cl}_2$  in the absence of  $\text{O}_2$  :-

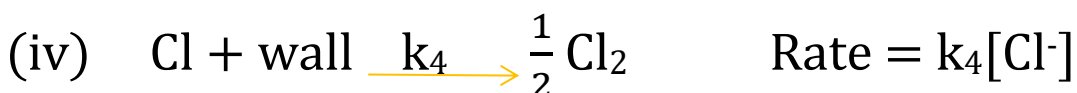
Initiation reaction:-



Chain propagation.



Chain termination.



Derivation of rate law:-

The total rate of formation of  $\text{HCl}$  is given by reaction (ii) and (iii)

$$\frac{d[\text{HCl}]}{dt} = k_2[\text{Cl} \cdot][\text{H}_2] + k_3[\text{H} \cdot][\text{Cl}_2] \longrightarrow (1)$$

The rate of formation of  $\text{Cl} \cdot$  atoms is given by steps (i) and (iii) and the rate of removal of  $\text{Cl} \cdot$  atoms is given by steps (ii) and (iv). Therefore, the net rate of formation of  $[\text{Cl} \cdot]$  atoms is given by.

$$\frac{d[\text{Cl} \cdot]}{dt} = k_1 \text{ Iabs} + k_3[\text{H} \cdot][\text{Cl}_2] - k_2[\text{Cl} \cdot][\text{H}_2] - k_4[\text{Cl} \cdot] \longrightarrow (2)$$

Similarly, net formation of  $\text{H} \cdot$  atoms can be written as -

$$\frac{d[H]}{dt} = k_2[H_2][Cl] + k_3[H][Cl_2] \longrightarrow (3)$$

Now, when the stationary state is reached, it following that.

$$\frac{d[H]}{dt} = \frac{d[Cl]}{dt} = 0$$

Therefore, equation (2) and (3) becomes as -

$$k_1 I_{abs} + k_3[H][Cl_2] - k_2[Cl][H_2] - k_4[Cl] = 0 \longrightarrow (4)$$

$$k_2[H_2][Cl] - k_3[H][Cl_2] = 0 \longrightarrow (5)$$

now, by adding equation (4) and (5) we have-

$$k_1 I_{abs} + k_4[Cl] = 0$$

or,  $k_4[Cl] = k_1 I_{abs}$ .

$$\text{Or, } [Cl] = \frac{K_1}{K_4} I_{abs} \longrightarrow (6)$$

Now, equation (5) can be written as-

$$K_2[H_2][Cl] = k_3[H][Cl_2] \longrightarrow (7)$$

Again, after substituting equation (7) in (1) we have-

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_2[H_2][Cl] = 2k_2[H_2][Cl] \longrightarrow (8)$$

Now, after substituting the value of [Cl] from equation (6) to (8) we have-

$$\frac{d[HCl]}{dt} = 2k_2 \frac{K_1}{K_4} I_{abs} [H_2]$$

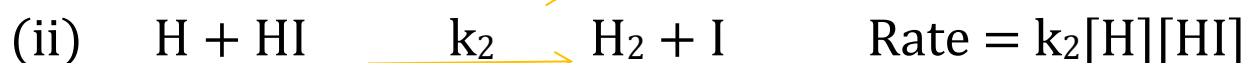
$$\text{Or, } \frac{d[HCl]}{dt} = \frac{2K_1K_2}{K_4} I_{abs} [H_2] \longrightarrow (9)$$

Equation (9) is in perfect agreement with experiment.

### Photochemical reaction of decomposition of HI

Or

### Kinetics of decomposition of HI





In the above mechanism the hydrogen iodide is consumed in equation (1) and (2). Thus, its rate of dissociation is given by

$$\frac{-d[HI]}{dt} = k_1 I_{abs} + k_2[H][HI] \longrightarrow (1)$$

Also, the net rate of formation of hydrogen atoms is given by

$$\frac{d[H]}{dt} = k_1 I_{abs} - k_2[H][HI] \longrightarrow (2)$$

Now, since [H] is short lived the steady treatment can be applied to it.

Thus,

$$\frac{d[H]}{dt} = 0 = k_1 I_{abs} - k_2[H][HI]$$

$$\text{Or, } k_1 I_{abs} = k_2[H][HI] \longrightarrow (3)$$

Now, from equation (1) and (3) we have-

$$\frac{-d[HI]}{dt} = 2k_1 I_{abs} \longrightarrow (4)$$

Now,

$$\text{Quantum yield} = \frac{\frac{-d[HI]}{dt}}{K_1 I_{abs}} = \frac{2K_1 I_{abs}}{K_1 I_{abs}} = 2$$

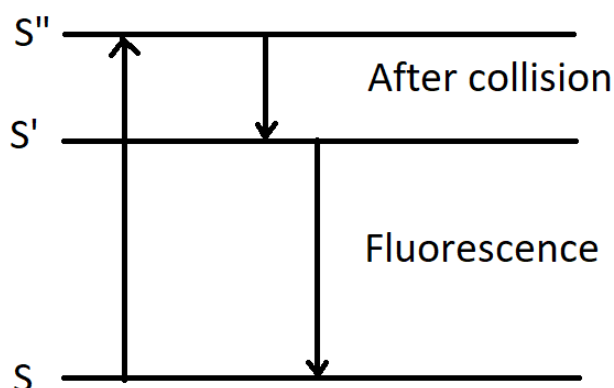
This value of quantum yield is in quite agreement with experimental value.

### Fluorescence:-

- Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation.
- In most cases, the emitted light has a longer wave length and therefore, lower energy, than the absorbed radiation.

- The absorbed energy shall be released within  $10^{-8}$  seconds but it may come out in successive stages.

➤ Explanation:-



Note :- Resonance radiation:- When an atom or molecule absorbs light, it is excited to higher energy level and the absorbed energy is emitted back within  $10^{-8}$  second and which has sum frequency, it is called as resonance radiation.



- This phenomenon is instances and starts immediately after the absorption of light and stops as soon as the incident light is cut off.
- Different substance absorbed light of different wave length.

Examples:-

- Fluorspar fluoresces blue light.
- Uranium glass fluoresces green light.
- Chlorophyll fluoresces red light.

- Quinine sulphate fluoresces blue light.

Applications:-

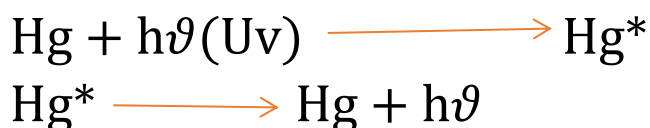
- (1) When Uv light is incident on newly laid eggs, they fluoresce with rosy colour, while bad eggs appear blue.
- (2) Butter, honey etc. can be readily distinguished.
- (3) The difference in the fluorescence caused by ultraviolet rays in different types of inks enables to detect forged documents.
- (4) Fluorescent lamps which are now widely used for lighting depend upon the fluorescence caused by Uv light on phosphorus coated inside the fluorescent tube.

Anti stokes Behaviour :- According to G.G Stoke, the emitted radiation in fluorescence has greater wave length than the absorbed radiations. There are however cases. Where stokes law is violated.

Two examples are –

(a) Resonance fluorescence:-

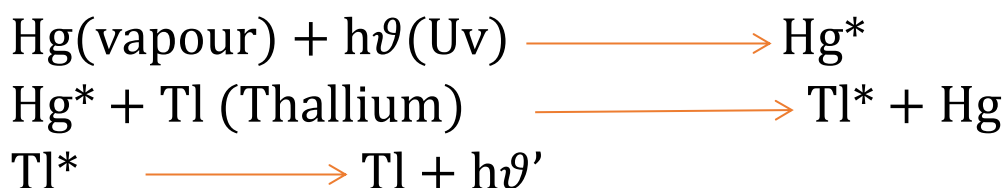
In certain cases, the fluorescent light has the same frequency as that of incident light. This fluorescent light is called resonance radiation and the phenomenon is known as resonance fluorescence.



(b) Sensitised fluorescence:-

A substance which is normally non – fluorescence may be made fluorescent in the presence of other fluorescent

substances this phenomenon is known as sensitised fluorescence.



### Quenching of fluorescence:-

When a photochemically excited atom has a chance to undergo collision with another atom or a molecule before it fluoresces, the intensity of fluorescent radiation may be diminished or stopped, this phenomenon is known as quenching of fluorescence.

Here, following changes may be possible –



This results in sensitised fluorescence.



Here,  $\text{H}_2$  molecule is activated.



Here, formation of a compound takes place.



Here, dissociation of  $\text{H}_2$  molecule takes place.

### Phosphorescence:-

The name phosphorescence has been derived from phosphorus. Which glows in dark but it is not phosphorescence.

It may be defined as –

“When light radiation is incident on certain substances, they emit light continuously even after the incident light is

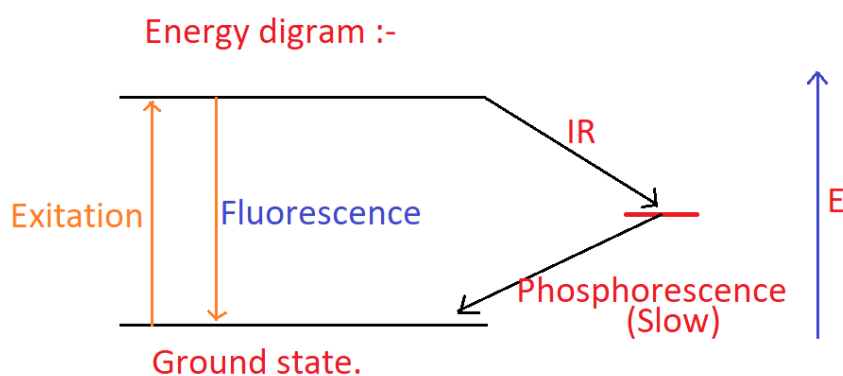
cut off. This type of delayed fluorescence is called as phosphorescence and the substances are called as phosphorescent substances”.

Ex – Sulphide of Ca, Ba and Sr etc.

ZnS, strontium aluminate.

### Some facts about phosphorescence are:-

- The phenomenon of phosphorescence is called chiefly by the Uv and violet parts of the spectrum.
- The phenomenon of phosphorescence is shown mainly by solids.
- The magnetic and dielectric properties of phosphorescent substances different before and after illumination.
- The time for which the light is emitted from phosphorescent substance depends upon the nature of substance and some time on temperature changes.



### Applications:-

Luminous paints contain about 2.5% alkali metal chlorides and a trace of heavy metal sulphides. Such a mixture is generally used for painting watch dials, electric switches etc.



### Lambert – Beer law:-

Lambert – Beer law is applicable those photochemical reaction which is in solution.

“When a monochromatic light of suitable frequency is passed through a solution. It is absorbed by the solution. As a result, the intensity of the light. When it finally emerges from the solution reduces”.

If,  $I_0$  = Intensity of incident light.

$I_t$  = Intensity of the transmitted light.

$I_a$  = Intensity of light absorbed by a solution.



$$I_a = I_0 - I_t \longrightarrow (1)$$

Intensity of the light is defined as the number of photons falling on unit area of a surface in present time.

The probability that the photons of beam of intensity  $I$  will be absorbed by the sample is directly proportional to the concentration and the thickness of the absorbing solution.

Thus,

$$\frac{dI}{I} \propto -c dx$$

$$\text{Or } \frac{dI}{I} = -\alpha c dx \longrightarrow (2)$$

Here,  $dI$  = Change in intensity

$dx$  = Thickness of solution

$c$  = Concentration of solution

$\alpha$  = Proportionality constant.

Here, (-) i.e sign is indicate that, there is decrease in intensity of light absorbed by the solution.

Now, after integration equation (2) we have.

$$\int_{I_0}^I \frac{dI}{I} = -\alpha c \int_0^b dx \longrightarrow (3)$$

$$\ln \left( \frac{I}{I_0} \right) = 2.303 \log \left( \frac{I}{I_0} \right) = - bc.$$