LAWS OF PHOTOCHEMISTRY

There are two basic laws governing photochemical reactions :

(*a*) The Grothus-Draper law

(*b*) The Stark-Einstein law of Photochemical Equivalence

Grothus–Draper Law

When light falls on a cell containing a reaction mixture, some light is absorbed and the remaining light is transmitted. Obviously, it is the absorbed component of light that is capable of producing the reaction. The transmitted light is ineffective chemically. Early in the 19th century, Grothus and Draper studied a number of photochemical reactions and enunciated a generalisation. This is known as **Grothus-Draper law** and may be stated as follows : **It is only the absorbed light radiations that are effective in producing a chemical reaction.** However, it does not mean that the absorption of radiation must necessarily be followed by a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy remains unused. It may be re-emitted as heat or light.

The Grothus-Draper law is so simple and self-evident. But it is purely qualitative in nature. It gives no idea of the relation between the absorbed radiation and the molecules undergoing change.

Stark-Einstein Law of Photochemical Equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reactions by application of *Quantum theory of light*. They noted that each molecule taking part in the reaction absorbs only a single quantum or photon of light. The molecule that gains one photon-equivalent energy is activated and enters into reaction. Stark and Einstein thus proposed a basic law of photochemistry which is named after them. The **Stark-Einstein law of photochemical equivalence** may be stated as :

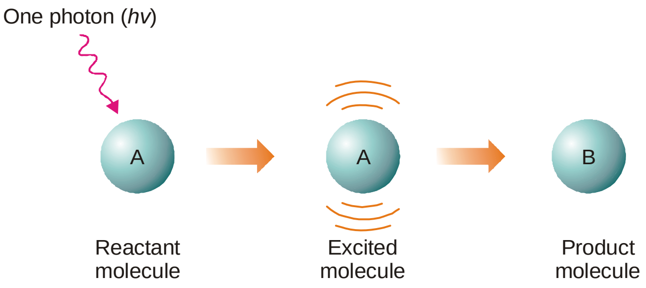

Figure 30.6
Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule.

In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products.

The law of photochemical equivalence is illustrated in Fig. 30.6 where a molecule 'A' absorbs a photon of radiation and gets activated. The activated molecule (A*) then decomposes to yield B. We could say the same thing in equational form as :

$$\begin{array}{lrcl} & A + h\nu & \longrightarrow & A^* \\ & A^* & \longrightarrow & B \\ \hline \text{overall} & A + h\nu & \longrightarrow & B \end{array}$$

In practice, we use molar quantities. That is, one mole of A absorbs one mole of photons or one einstein of energy, *E*. The value of *E* can be calculated by using the expression given below:

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

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 :

$$\begin{array}{rcll}
\text{HBr} + h\nu & \longrightarrow & \text{H} + \text{Br} & \text{Primary reaction} \\
\text{HBr} + \text{H} & \longrightarrow & \text{H}_2 + \text{Br} & \text{Secondary reaction} \\
\text{Br} + \text{Br} & \longrightarrow & \text{Br}_2 & \text{Secondary reaction} \\
\hline
2\text{HBr} + h\nu & \longrightarrow & \text{H}_2 + \text{Br}_2 & \text{Overall reaction}
\end{array}$$

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

$$\begin{array}{rcll}
\text{AB} + h\nu & \longrightarrow & \text{A} + \text{B} & \text{Primary} \\
\text{AB} + \text{A} & \longrightarrow & \text{A}_2 + \text{B} & \text{Secondary}
\end{array}$$

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.

$$\begin{array}{rcll}
\text{A}_2 + h\nu & \longrightarrow & 2\text{A} & \text{...(1)} \quad \text{Primary} \\
\text{A} + \text{B}_2 & \longrightarrow & \text{AB} + \text{B} & \left.\begin{array}{l}\text{...(2)} \\ \text{...(3)}\end{array}\right\} \begin{array}{l}\text{Secondary} \\ \text{Reaction chain}\end{array} \\
\text{B} + \text{A}_2 & \longrightarrow & \text{AB} + \text{A} &
\end{array}$$