B.Sc. (Honours) Part-III

Paper-VA

Topic: Law of Photochemistry

UG

Subject-Chemistry

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BASIC LAWS OF PHOTOCHEMISTRY

When a beam of radiant energy impinges upon matter, several types of interactions such as reflection refraction, diffraction, interference, absorption ect, may occur. Of these interactions absorption, in which certain frequencies are selectively removed by matter is of unique importance. The energy thus absorbed is transfered to atoms or molecules in matter. As a result, these atoms or molecules in the ground state are excited.

There are two basic laws governing photochemical reactions:

(*a*) **The Grothus-Draper law**

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

(a) 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 favorable 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.

(b) 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:

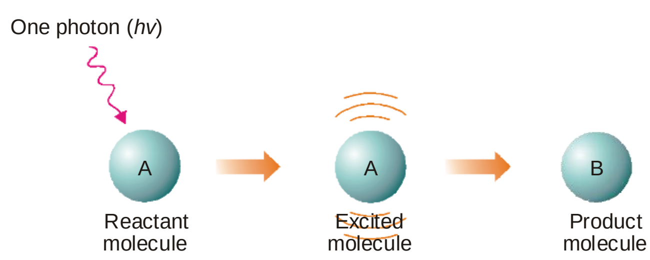

Figure 1 Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule.

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 :

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

$$A^* \longrightarrow B$$

overall $A + h\nu \longrightarrow B$

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:

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

The energy of photons; Einstein

We know that the energy of a photon (or quantum), E , is given by the equation. ...(1)

$$E = hv = \frac{hc}{\lambda}$$

where h = Planck's constant (6.624×10^{-27} erg-sec)

v = 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,

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

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

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

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

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

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

or

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

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.**