

A Review on Photochemistry and Spectroscopy

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ABSTRACT

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Photochemical reaction, a chemical reaction initiated by the absorption of energy in the form of light. The consequence of molecules' absorbing light is the creation of transient excited states whose chemical and physical properties differ greatly from the original molecules. These new chemical species can fall apart, change to new structures, combine with each other or other molecules, or transfer electrons, hydrogen atoms, protons, or their electronic excitation energy to other molecules. Excited states are stronger acids and stronger reductants than the original ground states. Spectrometric biosensors, which depend on the changes of photophysical properties, have been found to be particularly attractive, because of the fact that spectrometry is the most studied and most widely used technology. Now, with the development of nanoscience and nanotechnology, many nano-inspired spectrometric biosensors, including colorimetric sensors, fluorescent sensors, chemiluminescence sensors, electrochemiluminescence sensors, surface-enhanced Raman scattering sensors, and dynamic light scattering sensors, have emerged. These biosensors not only hold the inherent advantages of spectrometric analysis, but show their own unique advantages from the nanomaterials at the same time.

Keywords: Photochemical reaction, Photophysical properties, Spectrometric biosensors, Chemiluminescence, Nanomaterials.

I. INTRODUCTION

Photochemistry is the study of chemical reactions resulting from the exposure of light radiations. Light supplies the required energy to take place the photochemical reactions¹. The visible and UV radiations (2000-8000Å wavelength) are mainly used in photochemical reactions. *Thermochemical reactions* (dark reactions) are brought about by molecular collisions. These reactions are spontaneous

and are accompanied by a decrease in free energy. But certain photochemical reactions are accompanied by an increase in free energy. All *photochemical reactions* take place in two steps. In the first step, the reacting molecules are activated by absorption of light. In the second step, the activated molecules undergo a photochemical change. For example, in the combination of hydrogen and chlorine, the first step is²:



The activated chlorine atoms (Cl.) then undergoes chemical reaction. It is evident from the above reaction that the second step can occur in absence of light.

Characteristics of photochemical reaction

1. Photochemical reactions take place by absorption of light.
2. When a light composing number of colours is used, the photochemical reaction may not be initiated by all colours.
3. The free energy change of a photochemical reaction may be either negative or positive.

Laws of Photochemistry:

Grotthus-Draper Law (or) The Principle of Photochemical Activation

Grotthus-Draper law states that only the light which is absorbed by a substance can bring about a photochemical change. However, the absorbed radiation does not necessarily cause a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy may be reemitted as heat or light or it remains unused³.

Stark-Einstein Law of Photochemical Equivalence (or) Principle of Quantum Activation:

It states that in a primary photochemical process (first step) each molecule is activated by the absorption of one quantum of radiation (one photon). When a molecule absorbs a photon, it is not necessary that only one molecule should react. The absorption of one photon by a molecule is only the first step resulting in the formation of an activated molecule. This further may or may not react or may cause the reaction of many molecules through a chain mechanism.

Measurement of Absorbed Intensity

A photochemical reaction takes place by the absorption of photons of light by the reacting molecules. Therefore, it is essential to determine the intensity of light absorbed by the reacting molecules. Radiation emitted from a source of light, L (sun light, tungsten filament, mercury vapour lamp) is passed

through the lens, which produces parallel beams. The parallel beams are then passed through a monochromator, B, which yields a beam of the desired wavelength only. This monochromatic light is allowed to enter into the reaction cell, C, immersed in a thermostat, containing the reaction mixture. The part of the light that is not absorbed fall on a detector, X, which measures the intensity of radiation. The most frequently used detector is the chemical actinometer. A chemical actinometer is a device used to measure the amount of radiation absorbed by the system in a photochemical reaction. Using chemical actinometer, the rate of a chemical reaction can be measured easily. Uranyl oxalate actinometer is a commonly used chemical actinometer. It consists of 0.05 M oxalic acid and 0.01 M uranyl sulphate in water. When it is exposed to radiation, oxalic acid undergoes decomposition to give CO₂, CO and H₂O. The residual concentration of oxalic acid can be found out by titrating with standard KMnO₄. The amount of oxalic acid consumed is a measure of the intensity of radiation⁴.

Classification of photochemical reaction based on quantum yield

Based on quantum yield, the various photochemical reactions can be divided into three categories.

1. The reaction in which the quantum yield is a small integer like 1,2.
Examples:
 - a) Dissociation of HI & HBr;
 - b) Combination of SO₂ + Cl₂ and
 - c) Ozonisation of O₂.
2. The reaction in which the quantum yield is less than 1.
Examples:
 - a) Dissociation of NH₃, CH₃COCH₃ & NO₂;
 - b) Transformation of maleic acid into fumaric acid.
3. The reaction in which the quantum yield is extremely high.
Examples:
 - a) Combination of CO + Cl₂;
 - b) Combination of H₂ + Cl₂.

Processes of photochemical reactions

The overall photochemical reaction consists of

i) *Primary reaction* and ii) *Secondary reaction*.

i. In the primary reaction, the quantum of light is absorbed by a molecule „A“ resulting in the formation of an excited molecule⁵.

ii. In the secondary reaction, the excited molecules react further to give the product of higher quantum yield. $A^* \rightarrow B$

Photochemical Decomposition of HI

It takes place in the radiation of wave length between 2070 Å - 2820 Å. The quantum yield of the reaction is found to be closer to 2.0.

Energy Transfer in Photochemical Reactions

Photosensitizations and Quenching: In some photochemical reactions, the reactant molecules do not absorb radiation and no chemical reaction occurs. However, if a suitable foreign substance (called sensitizer), which absorbs radiation, is added to the reactant, the reaction takes place. The sensitizer gets excited during absorption of radiation and transfers its energy to the reactants and initiates the reaction⁶.

1. Photosensitization: The foreign substance absorbs the radiation and transfers the absorbed energy to the reactants is called a photosensitizer. This process is called photosensitized reaction (or) photosensitization. Examples,

i) Atomic photosensitizers : mercury, cadmium, zinc and

ii) Molecular photosensitizers: benzophenone, sulphur dioxide.

2. Quenching: When the excited foreign substance collides with another substance it gets converted into some other product due to the transfer of its energy to the colliding substance. This process is known as quenching.

Mechanism of Photosensitization and Quenching can be explained by considering a general donor (D) and acceptor (A) system. In a donor-acceptor system, the donor D (sensitizer) absorbs the incident photon and gets excited from ground state (S₀) to singlet state (S₁). Then the donor attains the triplet excited state (T₁ or

3D). The triplet state of the donor is higher than the triplet state of the acceptor (A). This triplet excited state of the donor collides with the acceptor produces the triplet excited state of the acceptor (3A) and returns to the ground state (S₀). If the triplet excited state of the acceptor (3A) gives the desired products, the mechanism is called photosensitization. If the products are resulted directly from the excited state of the donor (3D), then A is called quencher and the process is called quenching⁷.

Examples for photosensitized reactions:

1. Dissociation of hydrogen molecule: UV light does not dissociate H₂ molecule, because the molecule is unable to absorb the radiation. But, if a small amount of mercury vapour is added, dissociation of hydrogen takes place. Here Hg acts as photosensitizer.

2. Photosynthesis in plants: During photosynthesis of carbohydrates in plants from CO₂ and H₂O, chlorophyll of plants acts as a photosensitizer. The energy of the light absorbed by the chlorophyll (due to the presence of conjugation in chlorophyll) is transformed to CO₂ and H₂O molecules, which then react to form glucose. In the presence of light and chlorophyll. G₀ becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the G₀ for this reaction is +2875 kJ. Since G₀ is positive, the above reaction is not possible.

Photophysical Process

Generally atoms or molecules go to excited state by the absorption of suitable radiation. If the absorbed radiation is not used to cause a chemical reaction, it will be re-emitted as light of longer wavelength. This process is called as photophysical process.

Types of photophysical process: Photophysical process is of two types,

i) Fluorescence and

ii) Phosphorescence.

i) Fluorescence: When a molecule or atom absorbs radiation of higher frequency (shorter wavelength), it gets excited. Then the excited atom or molecule re-emits the radiation of the same frequency or lower

frequency within short time (about 10-8 sec.). This process is called fluorescence, stops as soon as the incident radiation is cut off. The substance which exhibits fluorescence is called fluorescent substance⁸.

Examples: CaF₂, uranium, petroleum, organic dyes like eosin, fluorescein), chlorophyll, quinine sulphate solution, vapours of sodium, iodine, mercury, etc.

Types of fluorescence.

a) Resonance fluorescence: If the excited atom emits the radiation of the same frequency, the process is known as resonance fluorescence. Example, when mercury vapour at low pressure is exposed to radiation of wavelength 253.7 nm, it gets excited. Subsequently, when it returns to its ground state, it emits radiation of the same frequency, which it absorbed.

b) Sensitized fluorescence: If the molecule is excited, due to the transfer of part of excitation energy from the foreign substance, it emits the radiation of lower frequency, the process is known as sensitized fluorescence. Example, if the mercury vapour is mixed with the vapours of silver, thalium, lead or zinc, which do not absorb radiation at 253.7 nm and then exposed to the radiation, a part of the excitation energy from mercury is transferred and gets excited to higher energy state. When it returns to its ground state, it emits radiation of lower frequency.

ii) Phosphorescence: When a substance absorbs radiation of higher frequency, the emission of radiation is continuous for some time even after the incident light is cut off. This process is called phosphorescence (or) delayed fluorescence. The substance which shows phosphorescence is called phosphorescent substance.

Examples: Zinc sulphide, alkaline-earth sulphides (eg. CaS, BaS and SrS).

Chemiluminescence

Chemiluminescence is a process in which visible light is produced by a chemical reaction at a temperature at which a black body will not give out visible radiation. Thus, chemiluminescence is the reverse of a

photochemical reaction. As the emission occurs at ordinary temperature, the emitted radiation is also known as "cold light". In a chemiluminescent reaction, the energy released during the chemical reaction makes the product molecule electronically excited. The excited molecule then emits radiation, as it returns to the ground state. Examples,

- The oxidation of ether solution of magnesium p-bromophenyl bromide gives rise to chemiluminescence, the greenish glow that accompanies the exposure of solution to air, being visible in day light.
- Glow of phosphorous and its oxide, in which the oxide in its excited electronic state emits light.
- When pyragallol is oxidized by H₂O₂, chemiluminescence is produced.
- The glow of fire flies is due to the chemiluminescence of a protein (luciferin) oxidation by oxygen in presence of an enzyme (luciferase)⁹.

SPECTROSCOPY

Spectroscopy is the study of the interaction of electromagnetic radiation with the matter. During the interaction the energy is absorbed or emitted by the matter. It is used to study the atomic and molecular structure of the substance.

Types of spectroscopy: Two types

- Atomic spectroscopy** deals with the interaction of the electromagnetic radiation with atoms. During which the atoms absorb radiation and gets excited from the ground state electronic energy level to another.
- Molecular spectroscopy** deals with the interaction of the electromagnetic radiation with molecules. This results in transition between rotational, vibrational and electronic energy levels.

Properties of Electromagnetic Radiation

Electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity. It requires no supporting media. An electromagnetic radiation is said to have a dual nature.

Wave properties of electromagnetic radiation

An electromagnetic radiation is an alternating electrical and associated magnetic force in space. Thus an electromagnetic wave has an electric component and magnetic component. The two components oscillate in plane perpendicular to each other.

- a) **Wavelength** is the distance between two successive maxima on an electromagnetic wave. It is denoted by the Greek letter lambda, (λ) (A beam carrying radiation of only one discrete wavelength is said to be monochromatic and a beam having radiation of several wavelengths is said to be polychromatic or heterochromatic)
- b) **Frequency** is the number of complete wavelength units passing through a given point in unit time.
Units : cycles/second or Hertz (Hz).
- c) **Wave number** is defined as the number of waves per centimeter in vacuum. unit : cm^{-1}
- d) **Velocity** (v): The product of wavelength and frequency is equal to the velocity of the wave in the medium.

ULTRA VIOLET and VISIBLE SPECTROSCOPY

The absorption of UV-Visible radiation by a molecule leads to transition among the electronic energy levels of the molecule and therefore it is called as electronic spectroscopy. All organic compounds absorb UV light.

*The region between 200 – 400 nm is near UV region
400 – 800 nm is visible region*

Below 200 nm is far (or) vacuum UV region

Absorption bands appear rather than absorption lines because vibrational and rotational effects are superimposed on the electronic transitions, so that an envelope of transitions arises¹⁰.

INFRARED SPECTROSCOPY

IR spectroscopy provides useful information about the structure of molecule quickly over the other methods. When infrared light is passed through a sample of an organic compound, some of the frequencies are absorbed while other frequencies are transmitted through the sample. If we plot the percent absorbance or transmittance against frequency, the result is an infrared spectrum.

Principle: Infrared spectra is produced by the absorption of energy by a molecule in the infrared region and the transitions occur between vibrational levels. So, IR spectroscopy is also known as vibrational spectroscopy.

Range of infrared radiation :

IR = $650 - 4000\text{cm}^{-1}$;

Far IR = lower than 650cm^{-1} ;

Near IR = higher than 4000cm^{-1}

Applications of IR spectroscopy

In the identity of the compounds and complexes. To ascertain hydrogen bonding in a molecule (as the dilution is increased, the absorption band, due to intermolecular hydrogen bonding diminishes while that due to intramolecular hydrogen bonding remains unchanged). In detecting impurities in a sample. It provides valuable information of molecular symmetry, dipole moments, bond lengths, etc. Distinguishing positional isomers of a compound. It is useful for identifying isomers. Eg. *cis*-alkenes 970cm^{-1} ; *trans*-alkenes $730 - 650\text{cm}^{-1}$. It may also be used for quantitative analysis of a mixture of compounds, in pollution detection, in milk analysis, etc¹¹.

II. CONCLUSION

One of the most venerable stories of discovery in synthetic chemistry is that of lumisantonin. The reaction, starting from the natural product santonin, was initiated by exposure to sunlight and is a stunning example of the dualistic simplicity and complexity often associated with photochemical reactions. This discovery inspired early organic photochemistry in the late 19th century and subsequently a truly remarkable structure elucidation. But perhaps the true impact was the inspiration of chemists in the mid-20th century to pioneer modern organic photochemistry through a multidisciplinary approach. In the decades following, there was a so-called "golden age" of photochemistry, where chemists learned to leverage photochemical reactivity in a

breathtaking variety of reactions, applying those reactions to enable groundbreaking syntheses. Potential applications of a variety of spectroscopic techniques to determine the interactions between minerals and reagents in flotation systems. To date it is found that infrared spectroscopy is the most successful and the relevant data in the literature is critically evaluated. X-ray photo-electron spectroscopy has also been successfully applied to study mineral—reagent interactions. The low-surface areas of minerals in flotation systems are a major limitation to the use of some spectroscopic techniques in studying the mineral surface. The suite of reagents used in flotation systems often imposes an additional complicating feature in obtaining relevant spectroscopic data about mineral surfaces. Nevertheless, spectroscopic studies used in the above manner, will continue to give a better understanding of the flotation process.

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