



Photochemistry

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Photochemistry, the branch of chemistry that deals with the chemical processes that are caused by the absorption of light energy. The process by which a photochemical reaction is carried out is called *photolysis*. Photolysis is usually initiated by infrared, visible, or ultraviolet light. A primary photochemical reaction is the immediate consequence of the absorption of light. Subsequent chemical changes are called secondary processes.

Photochemical reactions are utilized in synthetic chemistry to produce various organic molecules. In addition, many common processes are photochemical in nature and have important applications. For example:

Photosynthesis involves the absorption of light by the chlorophyll in plants to produce carbohydrates from carbon dioxide and water.

Photography uses the action of light on grains of silver chloride or silver bromide to produce an image.

Ozone formation in the upper atmosphere results from action of light on oxygen molecules.

Solar cells, which are used to power satellites and space vehicles, convert light energy from the sun to chemical energy and then release that energy in the form of electrical energy.

Historical Background

Important developments in the study of photochemistry occurred in the early 1800s. In 1817 the German physicist Theodor von Grotthus recognized that in order for light to be effective in producing a chemical change it had to be absorbed. In 1841 the American chemist John William Draper studied the reaction between moist hydrogen and chlorine gases. This reaction was observed first about 1801 and may have been the first recognized photochemical reaction. Draper noted that after a certain inhibition period the rate of the reaction was proportional to the intensity of the light absorbed. These observations led to the first law of photochemistry (the Grotthus-Draper law), which states that the amount of photochemical reaction is proportional to the quantity of light absorbed.

The development of the quantitative aspects of photochemistry began in earnest with the enunciation of the quantum theory by Max Planck in 1900 and its elucidation by Albert Einstein

in 1905. Planck, who is regarded as the founder of the quantum theory, espoused that an atom or a molecule can absorb only fixed quantities (quanta) of light energy. This energy, E , he theorized, is proportional to the frequency, f , of the light. The energy of a single quantum of radiation is given by

$$E = h f,$$

where h is a proportionality constant that was named "Planck's constant." Five years later Einstein proposed that light can be thought of as consisting of unusual particles called photons. Each photon of light is said to possess a quantum of energy given by the above relationship. These conclusions led to the second law of photochemistry, which states that the number of primary processes resulting from the absorption of light is equal to the number of photons absorbed. Exceptions to this rule sometimes occur.

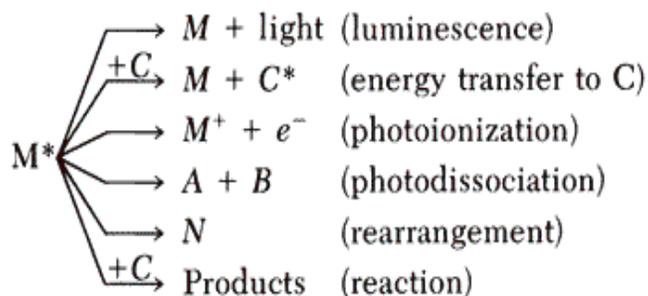
The Photochemical Process

To begin a photochemical process, an atom or molecule must absorb a quantum of light energy from a photon. When this occurs, the energy of the atom or molecule increases above its normal level. The atom or molecule is now in an excited (or activated) state. If a quantum of visible or ultraviolet light is absorbed, then an electron in a relatively low energy state of the atom or molecule is excited into a higher energy state. If infrared radiation is absorbed by a molecule, then the excitation energy affects the motions of the nuclei in the molecule.

After the initial absorption of a quantum of energy, the excited molecule can undergo a number of primary photochemical processes. A secondary process may occur after the primary step. The absorption step can be represented by $M \xrightarrow{\text{light}} M^*$ where the molecule M absorbs a quantum of light of appropriate energy to yield the excited M^* molecule.

Primary Photochemical Processes

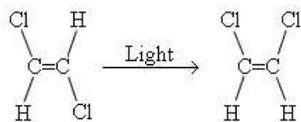
The figure below indicates the various primary processes that the excited M^* molecule can undergo:



The highly energized—or excited—molecule may return to its initial state according to any of three physical processes: 1) It can release its excitation energy by emitting luminescent

radiation through fluorescence or phosphorescence. 2) It may transfer its energy to some other molecule, C, with which it collides, without emitting light. The latter energy transfer process results in a normal molecule, M, and an excited molecule, C*. 3) As a result of the initial light-absorption step, an electron (e^-) in the atom or molecule may absorb so much energy that it may escape from the atom or molecule, leaving behind the positive M^+ ion. This process is called *photoionization*.

If the excited M^* molecule (or atom) does react, then it may undergo any of the following chemical processes: photodissociation, intramolecular (or internal) rearrangement, and reaction with another molecule C. Photodissociation may result when the excited molecule breaks apart into atomic and/or molecular fragments A and B. A rearrangement (or photoisomerization) reaction involves the conversion of molecule M into its isomer N—a molecule with the same numbers and types of atoms but with a different structural arrangement of the atoms. The conversion of *trans*-1,2-dichloroethylene into the *cis* isomer is an example of intramolecular rearrangement. The reaction is shown below:



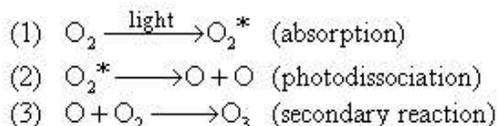
In the *trans* isomer the chlorine atoms lie on opposite sides of the double bond, whereas in the *cis* isomer they are on the same side of the double bond.

Secondary Photochemical Processes

Secondary processes may occur upon completion of the primary step. Several examples of such processes are described below.

Formation of Ozone

Ozone (O_3) is formed in the upper atmosphere from ordinary oxygen (O_2) gas molecules according to the reaction:

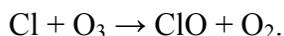


After a quantum of ultraviolet light is absorbed (step 1), the excited oxygen molecule dissociates into two oxygen atoms (step 2). An oxygen atom then reacts with O_2 to form ozone (step 3).

Destruction of Ozone in the Upper Stratosphere

Certain chlorofluoromethanes, such as CCl_3F and CCl_2F_2 , are used as refrigerants and—in some

countries—as propellants in aerosol cans. These compounds eventually diffuse into the stratosphere, where the molecules undergo photodissociation to produce chlorine (Cl) atoms, which then react with ozone molecules according to the formula

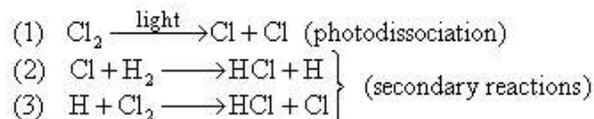


This decrease in the ozone content of the upper atmosphere allows more ultraviolet radiation to reach the surface of the earth.

Chain Reactions

If the primary photochemical process involves the dissociation of a molecule into radicals (unstable fragments of molecules), then the secondary process may involve a chain reaction. A chain reaction is a cyclic process whereby a reactive radical attacks a molecule to produce another unstable radical. This new radical can now attack another molecule, thereby reforming the original radical, which can now begin a new cycle of events.

The hydrogen-chlorine reaction is an example of a chain reaction. The overall reaction between hydrogen and chlorine gases in the presence of violet or ultraviolet light forms hydrogen chloride; it is given by $\text{H}_2 + \text{Cl}_2 \xrightarrow{\text{light}} 2\text{HCl}$. This reaction actually proceeds according to the following series of steps:



According to the above mechanism, a suitable quantum of light dissociates a chlorine molecule into atoms (step 1). The reactive Cl atom attacks a hydrogen molecule to yield hydrogen chloride and a hydrogen atom (step 2). The reactive hydrogen atom attacks a chlorine molecule, which regenerates the Cl atom (step 3). This chlorine atom can then react with another H_2 molecule according to step 2, beginning a new cycle of steps. Steps 2 and 3 will occur many times until either of the two reactants, H_2 and Cl_2 , is completely consumed or until the H or Cl radicals attack a new substance that has been introduced into the reaction chamber.

Quantum Yield

One of the most important quantitative measurements of a photochemical process is the quantum yield (or efficiency) of the reaction. It is a measure of the number of product molecules formed by the quantum of energy absorbed from each photon:

$$\text{quantum yield} = \frac{\text{product molecules}}{\text{photons absorbed}}$$

For primary processes, the quantum yield ranges from 0 to 1—an efficiency of 0% to 100%. For

secondary processes, the quantum yield can be greater than 1. For chain reactions, which produce many product molecules for every photon absorbed, the quantum yields can be as high as one million.

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