

A Brief Note on Photochemistry

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Brief Note

Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400–750 nm) or infrared radiation (750–2500 nm).

In nature, photochemistry is of immense importance as it is the basis of photosynthesis, vision, and the formation of vitamin D with sunlight. Photochemical reactions proceed differently than temperature-driven reactions. Photochemical paths access high energy intermediates that cannot be generated thermally, thereby overcoming large activation barriers in a short period of time, and allowing reactions otherwise inaccessible by thermal processes. Photochemistry is also destructive, as illustrated by the photodegradation of plastics.

Photochemistry that occurs in nature at or near the surface of the earth is due to the solar flux that reaches there. The spectral distribution of this radiation extends from about 350 nm to longer wavelengths. Shorter wavelengths are present high in the atmosphere, for example, causing O₂ photodissociation, which results in the protective ozone layer that is present in the stratosphere. Most photochemistry that occurs in nature at or near the surface of the earth is the result of visible or ultraviolet radiation; only in a minority of cases is near-infrared radiation involved.

Photochemical reactions of organic matter can take place in surface waters and any irradiated surfaces of organic or inorganic substrata. The prerequisite for photochemical reactions is the absorption of radiation. The photolytic ultraviolet (UV) and short wavelength visible radiation (~290–500 nm) is primarily responsible for abiotic photochemical reactions. In many surface waters, chromophoric dissolved organic matter (CDOM) dominates the absorption of photolytic solar radiation. In strict sense, CDOM is an optical definition for dissolved organic matter responsible for the absorption of solar radiation, but in this article CDOM is also treated as a representative organic matter having characteristics similar to humic substances.

Photochemical reactions proceed via a free-radical mechanism. The radicals, which are formed near the light source if they do not diffuse quickly to react, further with other species, will recombine, generating excess heat instead of a productive reaction. Large-scale photochemical reactions are usually performed with macro-scale lamps immersed in the reaction vessel. Issues involved in such design are scalability of light sources, heat and mass

transfer in the processes, and safety concerns (e.g., explosions caused by excess heat). Radical recombination reduces the quantum efficiency of the overall process. By PI miniaturization the diffusion length is reduced, leading to an increase in frequency of collision with other molecules to produce the desired product.

Photochemical reactions involving electromagnetic radiation in the UV-visible light range can induce structural changes in organic compounds. Direct photochemical reactions occur when the energy of electronic transition in the compounds corresponds to that of the incident radiation, with the compound acting as the light-absorbing molecule (i.e., chromophore). Hence, the structure of hydrocarbons determines the extent by which they are prone to photodecomposition, but photolytic half-lives are also significantly dependent on compound concentration and substrate properties (e.g., Behymer and Hites). In general, aromatic and unsaturated hydrocarbons are more prone to UV absorption and decomposition, with increasing numbers of conjugated bonds resulting in lower energy required for electronic transition.

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.

Photodissociation is not likely an important weathering mechanism for HMW straight-chain hydrocarbons, because these compounds do not absorb light efficiently. Nevertheless, these hydrocarbons may be transformed through the process of indirect photodissociation wherein another molecule (e.g., humic and fulvic acids) or substrate (mineral or organic) acts as the chromophore (NRC, 2002). Aromatic structures are prone to direct photochemical reaction in a manner that depends on molecular weight and degree of alkylation.

Photochemistry leading to high ozone episodes is triggered by local emissions of NO_x, mostly in the form of NO from combustion sources, and both natural and anthropogenic emissions of VOCs. Although NO at first suppresses ozone in the immediate vicinity of sources due to NO_x titration (NO + O₃ → NO₂ + O₂), its conversion to NO₂ eventually leads to ozone production further downwind. The efficiency of ozone production is partly determined by the relative abundances of NO_x and VOCs.

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