Answer on Question #73623, Chemistry / General Chemistry :

What are photosensitised chemical reactions? Explain giving suitable examples.

Solution.

Photosensitised reactions in solution generally prooeed by mechanisms involving free radicals and radical ions. The initial step in all these processes is the interaction between an electronically excited form of the light–absorbing molecule and a suitable acceptor molecule which must be present in the system. A number of different examples have been discussed, particularly those where (i) the initial processes are identical with the elementary process of the quenching of the fluorescence of the light–absorbing molecule and where the light–absorbing molecule undergoes transition to a triplet state which is capable of initiating the photosensitised reaction. Different compounds are used as photosensitizer such as ketones, aliphatic and aromatic amines, methylene blue, eosin, eosin yellow, rose bengal, acridin orange, chlorophyll, hematoporphyrin, carbazole, naphthalene and its derivatives, anthracene, riboflavin, dienes, hydroquinones, borohydride, mercury, ozone, H₂O₂, UV/H₂O₂, UV/O₃, UV/Fenton's reagent, organometallic complexes and many more compounds are reported as photosensitizer in different applications.

If only hydrogen gas is irradiated by ultraviolet light of λ = 253.70 nm the molecules do not dissociate to the atoms. But if the same radiation acts on hydrogen in presence of Hg-vapour, the hydrogen molecules undergo dissociation to the hydrogen atoms.

 $Hg + hv \rightarrow Hg^{-}$

 $Hg^+ + H_2 \rightarrow Hg + 2H$

The radiation excites the mercury atoms and the excited mercury atoms transfer the energy to the hydrogen molecules by collision. The reaction occurs as a result of transference of energy from pholochemically excited molecules by collision- in this case from Hg to H₂ molecules.



Another photosensitized reaction is the decomposition of oxalic acid in presence of uranyl sulphate.

 $UO_2^{2+} + hv \rightarrow UO_2^{2+*}$

 $\mathsf{UO_2^{2+*}+(COOH)_2} \rightarrow \mathsf{UO_2^{2+}+CO_2+CO+H_2O}$

The uranyl ion acts as a photosensitizer.

The decomposition of ozone in ordinary light by a trace of chlorine is an example of photosensitized reaction. In ordinary photographic films or plates silver bromide is the active ingredient which is decomposed by visible light of the shorter wavelength region. Thus red and orange bodies appear equally dark in the print. However, if suitable photosensitizes are mixed with the silver bromide the latter becomes sensitive to the entire part of the visible spectrum. Such films are known as panchromatic films. These give a more natural and livelier picture than the orthochromatic films.