

8.4: Photolysis

We have seen that the absorption of photons (especially in the ultraviolet-visible spectrum) is connected to the excitation of electrons. After excitation, a number of different relaxation pathways lead back to the ground state. Sometimes, absorption of a photon leads to a vastly different outcome. Instead of just relaxing again, the molecules may undergo bond-breaking reactions, instead.

An example of this phenomenon is observed in the complex ion $[\text{Co}(\text{NH}_3)]_6^{3+}$. Addition of UV light to this complex results in loss of ammonia. In the absence of UV light, however, the complex ion is quite stable.

In many cases, loss of a ligand is followed by replacement by a new one. For example, if an aqueous solution of $[\text{Co}(\text{NH}_3)]_6^{3+}$ is photolysed, an ammonia ligand is easily replaced by water.

Exercise 8.4.1

Draw a d orbital splitting diagram for $[\text{Co}(\text{NH}_3)]_6^{3+}$. Explain why this complex is normally inert toward substitution.

Exercise 8.4.2

Use the d orbital splitting diagram for $[\text{Co}(\text{NH}_3)]_6^{3+}$ to explain why this complex undergoes substitution upon irradiation with UV light

Photolysis is the term used to describe the use of light to initiate bond-breaking events. Photolysis frequently involves the use of high-intensity ultraviolet lamps. The high intensity light is needed in order to provide enough photons to get higher conversion of reactant into a desired product.

Two very different things could happen as a result of photon absorption. In one case, the molecule absorbs the photon, then somehow relaxes again, remaining unchanged overall. In the other case, the absorption of the photon results in bond cleavage and the formation of a new product. As a result, for every photon absorbed, there is a certain chance that the molecule will actually undergo a reaction, and a certain chance that the molecule will just relax again.

"Quantum yield" is an expression used to define the efficiency of a photolytic reaction. The quantum yield is just the number of molecules of reactant formed per photon absorbed. On a macroscopic level, we might say it is the number of moles of reactant formed per mole of photons absorbed.

Quantum yield = number of molecules of product formed / number of photons absorbed

The higher the quantum yield, the more efficient the reaction, because it requires less light in order to successfully form the product.

Exercise 8.4.3

Calculate the quantum yield in the following cases.

- 6 mmol of product results from absorption of 24 mmol of photons.
- 54 mmol of photons are required to produce 3 mmol of product.
- 1.2×10^{-6} moles of product are formed after absorption of 4.2×10^{-5} moles of photons.

In practice, determination of quantum yield is complicated because of the need to calculate exactly how many photons have been absorbed, in addition to how much product has been formed.

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