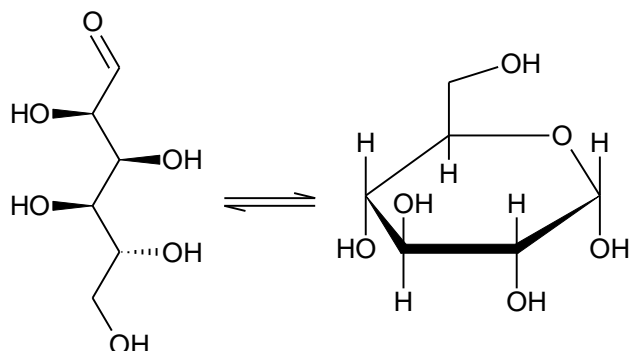


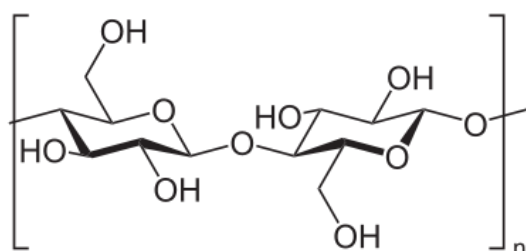
1. Cellulose and Cotton

1.1. Structure

The basic element of cellulose is D-Glucose, a molecule which shows an equilibrium between a linear and a ring type form.



D-Glucose-Pyranose, i.e. the ring form of D-glucose, can polycondensate to linear or branched polymers, which is called amylose, amylopectine or cellulose. Cellulose is a linear polymer, in which the D-glucose units are solely $\beta(1-4)$ -linked.



If several cellulose molecules are aligned to each other, rather stable fibers are obtained, which are essentially the main component of any kind of cotton as obtained from different plants. Beyond cellulose (91%), cotton comprises also water (~7.85%), protoplasm and pectins (0.55%), waxes and fatty molecules (0.4%), and mineral salts (0.2%).

1.2. Decomposition

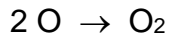
The decomposition of cotton concerns the degradation of waxes and fatty acids and in particular the depolymerisation or oxidation of the cellulose molecules.

Cellulolysis is the process of breaking down cellulose into smaller polysaccharides or completely into D-glucose units, which is thus a hydrolysis reaction. One has to keep in mind that D-glucose is an aldehyde, i.e. an aldose, which can be easily oxidised to gluconic acid, a carboxylic acid.

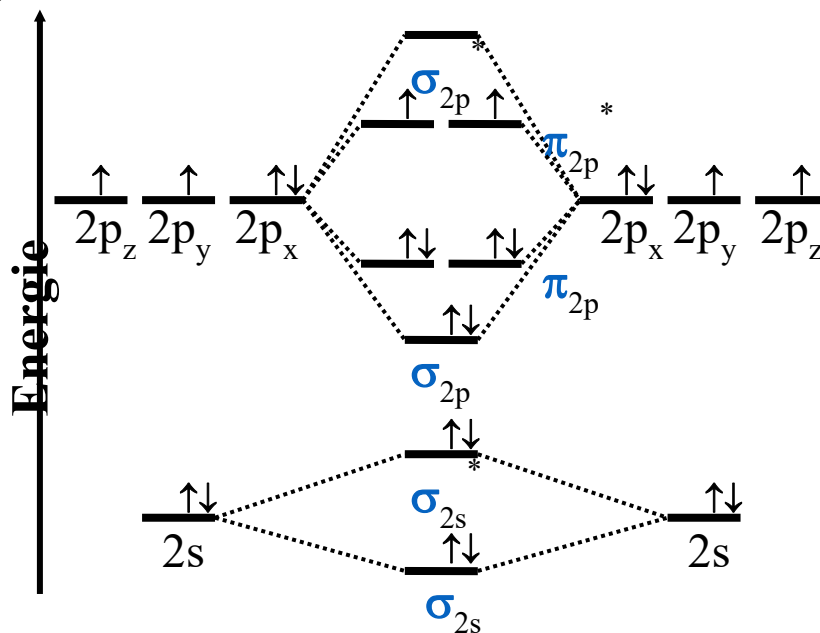
Because cellulose molecules bind strongly to each other, cellulolysis is relatively difficult compared to the breakdown of other polysaccharides and thus not very likely upon ambient conditions. The biochemical breakdown of cellulose is achieved by an enzyme, which is called cellulase and which allows certain species to metabolise cellulose and to use it as a source of energy.

2. Oxygen and its Photochemistry

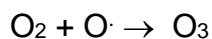
Atomar oxygen O (3P) is a biradical and thus extremely reactive, which results at ambient conditions in the immediate formation of molecular oxygen O₂.



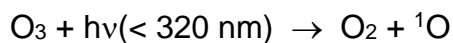
Molecular Oxygen O₂ in the electronic ground state ($^3\Sigma_g^-$) is a biradical too and thus paramagnetic. Its bond order is 2.0, which can be understood in the framework of the MO theory, and which explains the relatively low reactivity of molecular oxygen in the ground state:



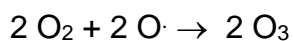
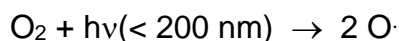
Dioxygen can further react to O₃ (ozone):



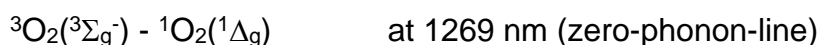
Ozone can be cleaved by UV-B and UV-C radiation, a process that occurs in the stratosphere, i.e. within the ozone layer.



The formation of Ozone, which takes place in the stratosphere and ionosphere, depends on the cleavage of Oxygen by VUV radiation. This is due to the fundamental absorption process of O₂ ($^3\Sigma_g^- - ^3\Sigma_u^-$) at 202.6 nm (zero-phonon-line), which is followed by its cleavage and the subsequent reaction of the resulting oxygen atoms with molecular oxygen to create ozone:



Molecular oxygen can also be photochemically activated without its subsequent cleavage. This process occurs in the NIR/IR range and results in the formation of singlet oxygen ($^1\text{O}_2$):



Singlet oxygen can add to C=C double bonds in a so called [2+2] cycloaddition, which is according to the famous Woodward-Hoffman rules photochemically allowed.

3. Photochemistry of Cellulose in the presence of Oxygen

Photooxidative degradation of cellulose results in a decrease of the degree of polymerization and α -cellulose content, concurrently producing chromophoric groups, namely, carbonyl, carboxyl, and hydroperoxide groups within the polymer. These groups are rather easily accessible for further redox processes.

References

- [1] ACD/ChemSketch Freeware, Version 10.02 (2006)
- [2] Paul D. Cooper, Robert E. Johnson, Terence I. Quickenden, *Planetary and Space Science* 51 (2003) 183 – 192
- [3] Wikipedia: Article Cellulose, Article Cotton
- [4] David N.-S. Hon, *Journal of Polymer Science: Polymer Chemistry Edition* 17 (1979) 441 - 454