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Mgr inż. Katarzyna KRUKIEWICZ – w 2011 r. ukończyła Wydział Chemiczny Politechniki Śląskiej, gdzie obecnie jest doktorantką. Należy do kolegium redakcyjnego miesięcznika CHEMIK, kwartalnika Chemik*light*. Jest autorką licznych artykułów popularno-naukowych, współautorką skryptu dla nauczycieli szkół średnich, współpracuje również z Uniwersytetem Dziecięcym „Unikids" prowadząc warsztaty chemiczne dla dzieci.

The phenomenon of singlet oxygen

Katarzyna KRUKIEWICZ – Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, Gliwice

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Oxygen in its pure form was discovered independently by Schele (1773) and Priestley (1774). However, it was Faraday who noticed that oxygen is attracted by magnet (1840). This observation was a first indication of the unusual electronic structure of molecular oxygen. In 1867 Fritzsche described the first process, in which the singlet oxygen was involved – the formation of a precipitation in a solution of 2,3-benzanthracene exposed to ambient light and air [1]. Nevertheless, the nature of this reaction was not recognized at that time.

The first evidence for a presence of a metastable and highly reactive form of oxygen was given by Kautsky and his co-workers in 1931 [2]. Three years later the lowest states of molecular oxygen were precisely defined via infrared spectroscopy measurements done by Herzbergs [3]. In 1944 singlet oxygen was deliberately used in the chemical synthesis for the first time, Schenck and Ziegler conducted the oxidation of -terpinene in the presence of chlorophyll and light leading to the formation of ascaridole [4].

Electronic structure and properties

In the ground state, molecular oxygen possesses of two electrons with parallel spins, which occupy π-antibonding orbitals that are perpendicular to each other [5]. The spin quantum number of this molecule equals 1, hence the paramagnetic can be observed. When the specific amount of energy is provided, these two electrons may rearrange and pair. In this case the spin quantum number has a zero value and the molecule is called singlet oxygen. Depending on the amount of energy absorbed by the molecule, two forms of singlet oxygen may be distinguished: singlet oxygen *delta* and singlet oxygen *sigma*. The energy difference between the ground state and the delta and sigma states are: 22.5 kcal mol^{-1} (energy corresponding to 1 eV) and 31.5 kcal mol^{-1}, respectively. Since the singlet oxygen is more electrophilic and has higher oxidizing properties than oxygen in its triplet state, it is consider as a versatile synthetic reagent. It may act as an oxidizing agent in chemical reaction or it may transfer the energy to other molecule in a process called physical quenching.

Generation

Singlet oxygen can be generated *via* two routes: the photosensitization and the dark reactions. The most important advantages of photosensitization are its simplicity and controllability [6]. The only requirements for this reaction are:

- source of oxygen, typically air is a good choice
- light of a proper wavelength range, usually ambient light is sufficient
- photosensitizer.

Photosensitizer is a molecule that is able to absorb light and transfer its excited state energy to molecular oxygen. As a result the singlet oxygen is formed. The sensitizer excitation is the one-photon transition between the ground state and excited state. The efficiency of this excitation is given by the quantum yield, which is the number of photons that are used to excite a sensitizer molecule to the number of photons absorbed by the system.

The commonly used photosensitizers are: phenothiazines (toluidine blue O, methylene blue, azure A), porphyrins (tetraphenylporphine, haematoporphyrin), phthalocyanines (phthalocyanine, zinc phthalocyanine tetrasulfonate), transition metal complexes (ruthenium(II) trisbipyridine, chromium(III) tris(2,2'-bipyridine)) and semiconductors (titanium dioxide).

The singlet oxygen can be also generated *via* chemical route, mainly the peroxide decomposition. This method is called dark reaction. The following dark reactions have been already described in the literature:

- dark reactions of calcium, molybdenum, tungsten and lanthanum peroxide perhydrates [7]

- the Murray's method: thermal decomposition of ozone-phosphite adducts [8]
- thermal decomposition of aromatic endoperoxides [8]
- decomposition of hydrogen peroxide with bleach [8].

Applications

The strong oxidizing power of the singlet oxygen can be utilized in the wastewater treatment. Phenol derivatives comprise one of the main classes of water pollutants, coming from paper and dye industry. The process of the phenols neutralization is well described in the literature: eosin, rose bengal, methylene blue, Zn(II) tetraphenylporphyrin and phthalacyanines [9], [10] have been applied as photosensitizers.

2-chlorophenol removal from wastewater was proposed by the group of the Lodz Technical University [11]. The main advantage of this new method is the application of oxygen from air and photons in visible range. Moreover, the immobilization of photosensitizer (rose bengal was used in this case) on silane gel carrier enables its recovery and reuse.

Singlet oxygen may also be used in various medical applications, like freshly frozen plasma decontamination [12]. The photosensitizer employed in all medical processes must be of high antimicrobial activity in addition to its non-toxicity for humans. These criteria are perfectly satisfied by methylene blue, a compound belonging to phenithiazines [13]. The mechanism of its action is based on the interaction between singlet oxygen and the nucleic acid, thus the reaction sequence involves the excitation of a dye molecule, formation of singlet oxygen and oxidation of electronegative moieties in nucleic acid, cell walls and enzymes [14]. A good adsorption of phenothiazine dyes, makes possible of the local antimicrobial therapy. Both methylene blue and toluidine blue O, have been already demonstrated to posses a high photoactivity against microorganisms such like *Helicobacter pylori, Escherichia coli, Staphylococcus aureus, Enterococcus faecium*, etc [13], [15].

Nowadays, a great number of phenothiazine derivatives (over 50 main structures) are being synthetized, since the modification of parent structure frequently leads to formation of a compound with significant biological activity [16]. Phenothiazine derivatives are sometimes called "antibacterial of the future" and thought to become a novel alternative to conventional antibiotics [17].

Translation into English by the Author

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Katarzyna KRUKIEWICZ – M.Sc., graduated from the Faculty of Chemistry, Silesian University of Technology, Gliwice (2011); currently being Ph.D. student at the same university. She was invited to join the editorial board of CHEMIK and Chemik light. She is the author of numerous popular scientific articles and co-author of a textbook for high-school teachers. She also holds the workshops on chemical experiments for children as a part of Children's University "Unikids".

Computational methods in chemistry - on the trail of the secrets of life

Computer prediction of the construction of biological systems based on their sequences may allow to skip the expensive and time-consuming experimental studies. Knowledge of such structures can help in designing drugs, argues Dr. Mariusz Makowski from the University of Gdańsk. The researcher improves computational methods in chemistry with particular emphasis on the methods of quantum mechanics. He explained in an interview with PAP that modern computational methods are not perfect, but allow to select the best test particles. This results in research costs reduction. In his assessment, these tests may help, and even sometimes replace experiments. For his work has received grants from: "Polityka", the Foundation for Polish Science, the Foundation for the Development of the University of Gdańsk, a team award of the Ministry of Education and Sport and the second degree Rector's Award. In his view, foreign fellowships allow to establish new scientific and social contacts. Researchers can often accomplish many tasks impossible in Poland due to lack of proper equipment. The researcher deplores the fact that many research centres in Poland are still unable to buy modern equipment due to the low level of funding allocated to science in our country. At Cornell University, Dr. Makowski joined the team of Prof. Harold A. Scheraga, who had been cooperating with the University of Gdańsk for more than 20 years, and, together with Prof. Adam Liwo from the University of Gdańsk Faculty of Chemistry developed a force field (equations describing the energy hypersurface) which will allow for predicting the structure of peptides and proteins. Dr. Makowski refines the selected part of the field.

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