

Chemiluminescence – mystery of cold light

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Please cite as: CHEMIK 2013, 67, 11, 1085–1096

Introduction

Luminescence phenomena, such as the aurora borealis, phosphorescence of the sea, luminescence of living organisms, phosphorescent wood or phosphor have fascinated man since ancient times. Aristotle was the first one who described “cold light” in dead fish, fungi and the luminous fireflies [1].

The term of luminescence was introduced in 1888 by E. Wiedemann. He stated that certain compounds are capable of emitting light without previous heating. Wawilow generalized this definition and stated that luminescence is the excess of the molecule light radiation over thermal radiation of the same molecule in the given spectral region and temperature. Luminescence is characterized by limited duration (do not stop immediately after excitation decay) [2].

Chemiluminescence is observed among aromatic and heterocyclic compounds including dyes (fluorescein, eozyn), biological compounds (chlorofil, carotenoid, certain vitamins and hormones) [3].

The current classification of luminescence phenomena is based on the categorization proposed by Wiedemann and depends on excitation mechanisms of molecule [4]. Luminescence phenomena are classified as follows:

- **Photoluminescence** – emission produced by the absorption of ultraviolet, visible or infrared radiation. Based on duration between absorption and emission of photons, fluorescence and phosphorescence are distinguished. The fluorescence occurs when time between absorption and emission of light is no longer than 10^{-8} s. If the time between absorption and emission of light is longer than 10^{-8} s the phosphorescence occurs
- **Thermoluminescence** – emission from solids induced by heating
- **Candoluminescence** – emission from incandescent solids
- **Triboluminescence** – emission induced by shaking, rubbing or crushing substance
- **Crystalloluminescence** – emission from crystallization
- **Electroluminescence** – emission from electrical discharges
- **Sonoluminescence** – emission from exposure to ultrasonic waves in solution
- **Bioluminescence** – emission from living organisms or biological systems (glowworm, bacteria, fungi, crustaceans)
- **Oxyluminescence** – emission from polymers induced by oxidation
- **Electrogenerated chemiluminescence** – emission produced at an electrode surface
- **Chemiluminescence** – emission of the ultraviolet, visible or near infrared radiation by molecules or atoms resulting from chemical reactions. Chemiluminescence takes place at room temperature in gas, liquid and solid phase [3].

In 1877 Polish scientist Radziszewski reported the chemiluminescence which was exhibited by the synthetic organic compound lophine (2,4,5-triphenylimidazole). He found that lophine emitted green light upon reaction with oxygen in the presence of strong base [5].

In general, two types of chemiluminescence mechanisms are distinguished (Fig. 1).

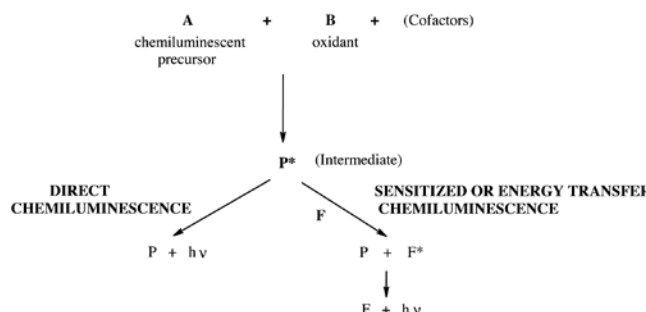


Fig. 1. Types of chemiluminescent reactions

In a direct reaction a substrate (A) and an oxidant (B) in the presence of cofactors react to form an intermediate product in an electronically excited state which relax to the ground state with photon emission.

An alternative for compounds producing ultraweak chemiluminescence is indirect sensitized chemiluminescence based on an effective energy transfer process from the excited species (P*) to a fluorophore (F) that after excitation is released to its ground state with photon emission.

Therefore the substrate (A) is responsible for light emission or acts as the energy transfer donor. The catalysts, enzymes or metal ions, reduce the activation energy and update chemiluminescence efficiency. Cofactors convert the substrates into a form capable of reacting and interacting with the catalyst to provide efficient leaving groups.

The excitation is a decisive step in chemiluminescent processes. Spontaneous light emission during reaction requires the presence of the following conditions. First, the reaction must be highly exothermic (40–70 kcal/mol) in order that the chemiluminescence occurred in the visible region (400–750 nm). This condition is related with redox reactions in the presence of oxygen and hydrogen peroxide or similar oxidants. Some of the energy produced must be channeled into a reaction pathway in which at least one of the upper vibrational levels of the reactants (probably corresponding to the transition state of the initial reaction) has the same energy and a comparable geometrical structure as an upper vibrational level of the lowest excited singlet state of a emissive product of the reaction. Second, chemiluminescence will occur when $\Delta H_a^* \leq \Delta H_a$, in which ΔH_a is the enthalpy of activation for “dark” reaction competing with the chemiluminescent pathway, whose enthalpy of activation is ΔH_a^* . Additionally, the lowest excited singlet state of the fluorophore has the same geometrical configuration as the ground electronic state of the reactant.

Chemiluminescence quantum yield is the parameter which determines the intensity of emission of light. In order the efficiency of the chemical energy transfer into chemiluminescence reaction (ϕ) was significant, the equation 1 must be preserved:

$$\phi = \phi_C \times \phi_E \times \phi_F \quad (1)$$

where:

ϕ_C – the chemical yield of excited product formation

ϕ_E – the excitation yield

ϕ_F – the quantum yield of fluorescence of the light-emitting species

The quantum yield of chemiluminescence depends on the efficiency of the particular intermediate processes leading to the emission of light. Chemiluminescence emission is influenced by factors such as: the chemical structure of the chemiluminescent precursor, the nature and concentration of other substrates affecting the process and favoring other irradiative competition processes, the selected catalyst, the presence of metal ions, especially transition metals involved in the processing of the oxidant, the presence of energy transfer acceptors, temperature, pH, ionic strength and the type of the solvent. Molecules that are involved in chemiluminescence reactions (luminogenic compounds) are generally reduced species, such as molecules containing amino and hydroxyl groups and polycyclic aromatic ring systems [3].

Liquid-phase chemiluminescence reactions

There are known numerous chemical reactions in which emission of light occurs. The most known are oxidation reactions by oxygen or hydrogen peroxide usually in the presence of catalyst – enzyme. The representative example is oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) in basic solution and in the presence of catalyst (Fig. 2).

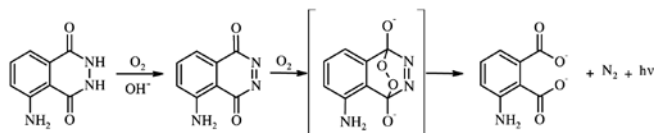


Fig. 2. Oxidation of luminol in the presence of hydrogen peroxide and catalyst

The oxidation of luminol often occurs in the presence of hydrogen peroxide and catalysts such as $(\text{Fe}(\text{CN})_6)^{3-}$, $\text{Cu}(\text{II})$ or $\text{Co}(\text{II})$ in basic solution. A dianion of luminol is formed as a key intermediate. It reacts with oxygen or an alternative oxidizing agent to yield an excited state of the aminophthalate ion that is responsible for the emission of blue light in water and yellow-green in DMSO [6, 7]. The oxidation of luminol in basic solution is one of the best known and most efficient chemiluminescent reaction. A quantum yield of chemiluminescence in water and DMSO is of about 1–1.5% and up to 5%, respectively [8, 9]. The luminol reaction is used in direct assays for the determination of different oxidizing agents such as H_2O_2 , O_2 , I_2 and in indirect assays for determination of glucose in the presence of enzymes such as peroxidase; metal ions and their complexes ($\text{Cu}(\text{II})$, $\text{Co}(\text{II})$, $\text{Fe}(\text{III})$ etc.) and inhibitors ($\text{Ag}(\text{I})$, $\text{Ce}(\text{IV})$, $\text{Ti}(\text{IV})$ etc.) [3].

Direct chemiluminescence is observed among limited group of organic compounds. These include indoles I [10], polydimethylaminoethylenes II [11] and Schiff's bases III [12] (Fig. 3).

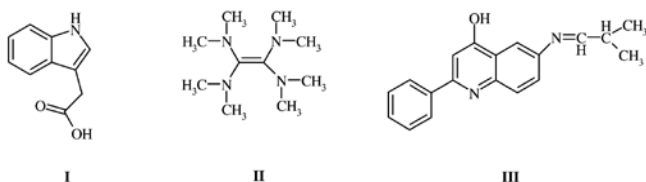
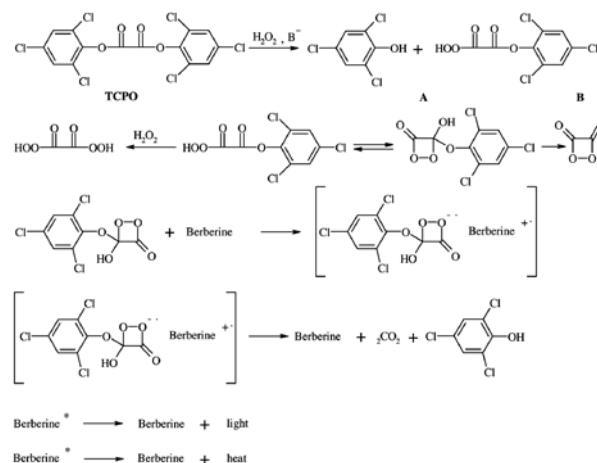


Fig. 3. Structure of direct chemiluminescent compounds

Another group of the most efficient chemiluminescence systems are peroxyoxalate derivatives (PO-CL) first reported in 1963 by Chandross [13]. The oxidation of oxalic acid derivatives with hydrogen peroxide in the presence of a fluorophore (9,10-diphenylanthracene) gave bright, long-lasting emission of blue light. The most frequently used oxalate derivatives are *bis* (2,4-dinitrophenyl) oxalate (DNPO) and *bis* (2,4,6-trichlorophenyl) oxalate (TCPO). A typical PO-CL system consists of the oxalate derivatives, hydrogen peroxide as oxidant and catalyst. The

intermediate products obtained in chemiluminescence are capable of producing an excited state of fluorophore responsible for emission of light. The example of sensitized peroxyoxalate chemiluminescence in the presence of berberine is presented in Figure 4.



where: B⁻ sodium salicylate

Fig. 4. Mechanism of sensitized peroxyoxalate chemiluminescence in the presence of berberine

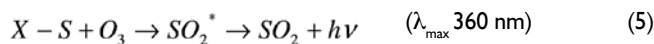
In chemiluminescence reaction the high-energy cyclic intermediates (dioxetane species A, B) are suggested. Excited molecule of fluorophore (berberine) emits intense yellow light via the chemically initiated electron exchange luminescence (CIEEL) mechanism [14].

The oxidation of oxalate esters in the presence of diluted anhydrous hydrogen peroxide, catalyst – sodium salicylate and sensitizers has practical application in Cyalume Technologies products known as chemical light sticks. High quantum yield of sensitizers lightening reached several dozen percent have essential influence on commercial success of the chemical light sticks. These products find several practical applications in military, police, emergency services but also in floats for fisherman, sports, tourism and entertainment.

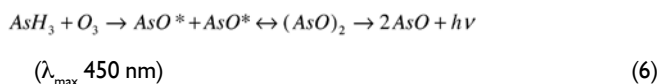
Cyalume products are environmentally friendly, safe, non-toxic, non-flammable, non-breakable, weather conditions resistant and completely waterproof. Chemical light sticks are disposable, stop lightening after a determined time. The elastic tube flashlight filled with hydrogen peroxide and a breakable capsule with oxalate esters and sensitizers is subsequent practical development introduced by American Cyanamid Company. Chemiluminescence reaction is observed after snapping inner capsule and shaking the tube when the reagents are mixed together. Time of shining such flashlight depends on the composition and exploitation and last from 5 minutes to 12 hours [15].

Another efficient chemiluminescence compounds are acridine esters derivatives. Intense blue-green chemiluminescence during the oxidation of lucigenin (10,10'-dimethyl-9,9'-bisacridinium dinitrate) with hydrogen peroxide or oxygen in the presence of catalysts such as $\text{Co}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Fe}(\text{III})$, $\text{Cu}(\text{II})$, $\text{Cr}(\text{III})$, or $\text{Ni}(\text{II})$, in alkaline solution, was first observed by Glue and Petsch in 1935. Mechanism of chemiluminescence of acridinium dimethylphenyl esters are presented in Figure 5.

Light emission from acridinium dimethylphenyl esters is generated in two steps. First, an initial treatment with acid rapidly converts the non-chemiluminescent pseudobase (A) to the chemiluminescent acridinium ester (B). Reaction of the acridinium ester (B) with alkaline hydrogen peroxide in the presence of cationic surfactant (cetyltrimethylammonium chloride) generates rapid chemiluminescence (< 5s). Excited state acridone (F) is believed to be the light emitting species in the chemiluminescence of acridinium phenyl esters. It is formed from decomposition of a high energy dioxetanone intermediate (E) or in direct formation from the dioxetane (D). Decomposition of the dioxetane intermediate (D)



Arsenic is the most abundant element in the terrestrial crust [58]. Arsenic compounds can be found especially in groundwater used for drinking but also in seas, rivers, soils, air and in food resources [59, 60]. The hydride of arsenic (AsH_3) is particularly toxic. Chemiluminescence of arsenic oxide in the presence of ozone for the first time was observed by Fujiwara et al. [61]. As a result of the reaction of AsH_3-O_3 system a broad emission band is observed ranging from 350 to 600 nm centered at 450 nm (equation 6). Numerous detection techniques of arsenic hydride measurement in ozone-induced chemiluminescence were reported [62–64].



Solid phase chemiluminescence

Some polymers exhibit weak chemiluminescence in the visible range when heated up in the presence of inert gas (air or oxygen). For the first time this phenomenon was observed by Ashby in 1961 from polypropylene [65]. Later, many important papers on chemiluminescence from polyolefins and polyamides [66–68], cellulose and biopolymers [69–73] were published. Emission of light during oxidation of polymers is called oxyluminescence [65] or oxychemiluminescence [74]. For chemiluminescence of polymers to be observed, oxygen must be present in the process [75–78].

Oxidation (autooxidation) is one of the most important processes responsible for degradation of polymers (Fig. 6) [79]. The first step (initiation) is the formation of primary radicals R^\cdot as a result of degradation of polymer materials by factors such as heat, light, catalysts (such as transition metals), radical initiators or impurities in the monomers. Radicals R^\cdot obtained rapidly react in the presence of oxygen to form peroxy radicals ROO^\cdot , which abstract hydrogen from the monomer and form an alkyl radicals R^\cdot and a hydroperoxides $ROOH$. Radicals generated from hydroperoxides $ROOH$ decompositions again abstract hydrogen atoms. New macro radicals produce a variety of product species in an another autooxidation cycle process.

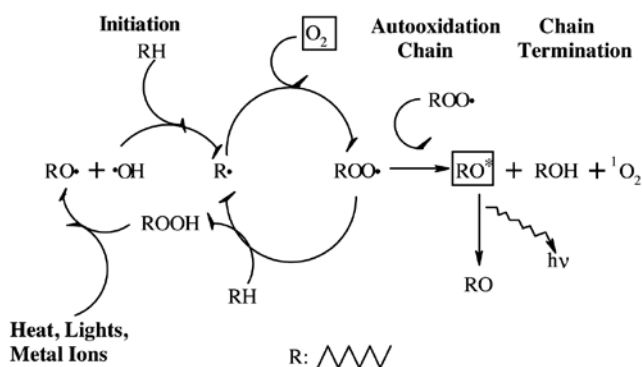


Fig. 6. The cycle of autooxidation

Termination of the propagation occurs in radical recombination reaction. When the oxygen pressure is suitably high, the termination occurs according to Russell mechanism (Fig. 7). As a result of bimolecular termination reaction of primary and secondary peroxy radicals an intermediate tetraoxide is obtained. Strongly exothermic (462 kcal/mol) the triplet ketone, singlet oxygen and alcohol are generated during its decomposition. Excited ketone emitting blue-violet (400–500 nm) light is the source of chemiluminescence emission from polymer [80, 81]. The termination mechanism was supported in other experiments concerning oxidation of hydrocarbon [82, 83].

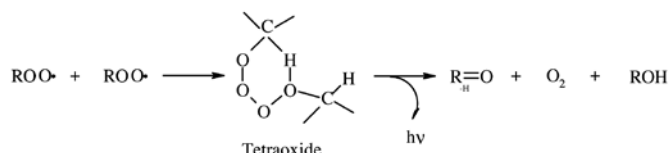


Fig. 7. Russell mechanism of chemiluminescence pathway

Peroxy radicals ROO^\cdot produced during decomposition of hydroperoxide are key intermediate in oxychemiluminescence [69, 84, 85]. Extensive research of chemiluminescence from polymers proved that various chemical and physical methods of excitation of polymer during heating are possible [86, 88]. Chemiluminescence can be induced by easily decomposable radical initiators introduced in polymeric materials [89, 90]. Recently, photo-induced chemiluminescence in the presence of xanthenes and triphenyl methane dyes have been reported [91]. Solid-phase chemiluminescence can be also used to evaluate the degree of degradation [92], to study the reaction mechanisms and oxidation kinetics [93, 94] or to assess the stabilization efficiency of additives such as antioxidants [95].

Summary

Nowadays, it is general tendency in analytical chemistry to detect various species at extremely low concentration (in the range of femtomol). This trend is connected with environmental requirements that influenced the reduction of large amount of waste and pollutants generated in analytical processes. Chemiluminescence as an environmentally friendly method fulfills ecological prerequisite. It is of great importance because it provides high sensitivity and selectivity detection system.

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Translation into English by the Author

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