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Light-created chemiluminescence

R F Vasil'ev, Yu B Tsaplev

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Abstract. The results of studies of light-created chemiluminescence are described systematically. Conditions for the transformation of a dark chemical reaction into a chemiluminescence reaction are considered. Examples of photosensitised and photoinduced processes as well as of analytical applications are given. The bibliography includes 161 references.

I. Introduction

In darkness at ambient temperatures, electronic excitation of molecules involved in chemical reactions is not a routine event. However, if such an event happens, it has a reliable witness, namely, light emission. No matter how intricate and unclear the chemical processes in the reactor may be, the observation of chemiluminescence (CL) unambiguously points to electronic excitation. Chemiluminescence is a remarkable example of the conversion of chemical energy into light energy. Electronic excitation in the chemiluminescence is due to the energy liberated in an elementary act of the reaction on the way from the activated state to the products and, broadly speaking, is rather improbable. Correspondingly, relatively few chemiluminescence reactions are known.

It can be assumed that the effect of light on reactants or a reaction mixture (*i.e.*, the delivery of additional energy) will allow overcoming the energy limitations and transform a dark reaction into chemiluminescence. Indeed, over the last 40 years compounds have been found that, being preliminarily illuminated, give rise to CL. The diversity of such systems is associated with the variety of types of interaction of light with matter and their different chemical consequences.

This review is aimed at the systematisation of the results of studies of light-created chemiluminescence systems, their classification and the refinement of terminology used for their description. The latter problem is associated with the fact that along with already accepted terms, for example, photosensitised CL, photochemiluminescence and light-induced CL, exotic terms such as optically pumped CL, photostoragechemiluminescence, *etc.*, are encountered.

The interaction between reactants that constitute a chemiluminescence system results in the electronically excited products or intermediates and light emission; this is why all starting components of a chemiluminescence system are justly referred to as chemiluminescent reactants. Among the components of a liquid-phase chemiluminescence reaction, one can single out a reactant that according to its composition and structure is the precursor of the primarily excited species and the light emitter.† It is this reactant that brings in individual features into the chemiluminescence system. To distinguish it from other reactants, it is called 'chemiluminophore'.‡ For liquid-phase CL, molecular oxygen [its concentration in aerated solutions varies from 0.2 (in H_2O) to 4 mmol litre^{-1} (in Et_2O)] and the solvent are the key reactants.

The present review deals with photosensitised oxidation of chemiluminophores with molecular oxygen. Attention is focused on chemiluminophores obtainable from precursors by photochemical mechanisms involving oxygen and solvent, as well as on chemiluminescence systems in which the light-induced intramolecular rearrangement of a molecule occurs.

II. Photosensitised chemiluminecence

Molecules and supramolecular structures can store for a while the energy of absorbed light quanta, being converted into the electronically excited state. The excitation energy is usually lost upon non-radiative transition of the molecule into its ground state; however, in certain cases the energy can be emitted as a luminescence quantum or transferred to other molecules, namely, quenchers. In the latter case, luminescence of the primary excited compound is quenched. The question of what happens if dissolved oxygen acts as the quencher, was raised by Kautsky back in the 1930s.[5] The studies of luminescence quenching with oxygen led to the discovery of singlet oxygen[6] and gave rise to a concept of 'active oxygen forms' (species $OH^{\bullet}$, $O_2H^{\bullet}$, $O_2^{-\bullet}$, $^1O_2$). Combined studies of photooxidation[5] and chemiluminescence, which, as a

R F Vasil'ev, Yu B Tsaplev N M Emanuel Institute of Biochemical Physics, Russian Academy of Sciences ul. Kosygina 4, 119991 Moscow, Russian Federation. Fax (7-495) 137 41 01, tel. (7-495) 939 73 58, e-mail: vasilev@sky.chph.ras.ru (R F Vasil'ev), tsap_04@mail.ru (Yu B Tsaplev)

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† For chemiluminescence reactions in the gas phase, such a reactant can be singled out only in rare cases, *e.g.*, in reactions involving volatile low-molecular dioxetanes, whereas the involvement of all reactants of the chemiluminescence system 'on equal terms' is typical.

‡ This term, which was introduced by analogy with 'luminophores', *i.e.*, substances that emit light upon activating radiation, is encountered with increasing frequency in the literature (see Refs 1 – 4).

rule, was observed in the oxidation,[7] initiated studies on the phenomenon of photosensitised chemiluminescence (PSCL).

1. Photooxidation

IUPAC defines photooxidation as the oxidation reactions initiated by light. In a more general form, these are the reactions in which a reactant loses an electron upon the absorption of a photon and also the light-induced reactions of substances with oxygen (a process in which a chemical bond is formed between oxygen and the substance is called photooxygenation).

Two types of photosensitised oxidation processes in liquid phase are distinguished.[8] Type I processes include reactions of the substrate (RH, R) with a sensitiser in the electronically excited triplet state (^{3}S), or photoionisation reactions. Type II processes correspond to the interaction of an electronically excited sensitiser with an oxygen molecule. Each type includes reactions of several kinds (Table 1).

Table 1. Classification of photosensitised oxidation processes.

Type I	Type II
a. Free-radical oxidation $^1S_0 + h\nu \longrightarrow {}^1S^* \longrightarrow {}^3S$, $^3S + RH \longrightarrow SH^{\bullet} + R^{\bullet}$, $(R^{\bullet} + {}^3O_2 \longrightarrow ROO^{\bullet})$	a. Oxidation involving singlet oxygen $^1S_0 + h\nu \longrightarrow {}^1S^* \longrightarrow {}^3S$, $^3S + {}^3O_2 \longrightarrow {}^1S_0 + {}^1O_2$, $RH + {}^1O_2 \longrightarrow$ products
b. Oxidation with electron transfer $^1S_0 + h\nu \longrightarrow {}^1S^* \longrightarrow {}^3S$, $^3S + R \longrightarrow S^{-\bullet} + R^{+\bullet}$, $(S^{-\bullet} + {}^3O_2 \longrightarrow S + O_2^{-\bullet}$, $R^{+\bullet} + O_2^{-\bullet} \longrightarrow$ products)	b. Oxidation with electron transfer $^1S_0 + h\nu \longrightarrow {}^1S^* \longrightarrow {}^3S$, $^3S + {}^3O_2 \longrightarrow [{}^1S_0 \cdots {}^1O_2]? \longrightarrow$ $\longrightarrow S^{+\bullet} + O_2^{-\bullet}$, $RH + O_2^{-\bullet} \longrightarrow$ products
c. Single-photon ionisation $^1S_0 + h\nu \longrightarrow S^{+\bullet} + e^-$,	c. Oxidation to form a biradical $^1S_0 + h\nu \longrightarrow {}^1S^* \longrightarrow {}^3S$, $^3S + {}^3O_2 \longrightarrow {}^{\bullet}SOO^{\bullet}$, $RH + {}^{\bullet}SOO^{\bullet} \longrightarrow$ products
or two-photon inonisation $^1S_0 + h\nu \longrightarrow {}^1S^* \longrightarrow {}^3S$, $^3S + h\nu \longrightarrow S^{+\bullet} + e^-$	

Note. $^1S_0$, $^1S^*$, ^3S are ground (non-excited), excited singlet and triplet states of the sensitiser molecule, respectively. In parentheses, the possible subsequent reactions are shown.

Several relatively simple tests allow one to determine the type of a photosensitised oxidation process in a system under study.

(1) The formation of singlet oxygen is inhibited by quenchers among which 1,4-diazabicyclo[2.2.2]octane (DABCO), carotenoids and sodium azide are the most popular.

(2) Radical processes are sensitive to scavengers, *i.e.*, traps of free radicals.

(3) Free-radical oxidation depends on the temperature, whereas oxidation that involves singlet oxygen is temperature independent.

(4) Involvement of singlet oxygen in the oxidation reaction can be confirmed by an independent synthesis using singlet oxygen formed in a chemical reaction [*e.g.*, from triphenyl phosphite ozonide $P(OPh)_3O_3$].

(5) Reactions that involve a superoxide ion are sensitive to superoxide dismutase.

(6) Reactions that involve solvated electrons are sensitive to the presence of N_2O (trap).

The phenomenon of sensitisation, which is associated with the enhanced reactivity of a molecule in the excited state, occurs also when the substrate itself plays the role of the sensitiser (S = RH). In this case, the process is referred to as autosensitisation.

2. Pigments and dyes

In 1951, persistent afterglow of chlorella photosynthesising cells following their illumination at 420–700 nm was discovered.[9] Studies of this phenomenon were continued with simpler objects. It was noticed [10] that red CL observed upon mixing of a chlorophyll solution with a formaldehyde solution in alkaline methanol, becomes more intense when the reaction mixture has been illuminated. Persistent afterglow was also observed [11] in aerated solutions of chlorophyll and pheophytin.

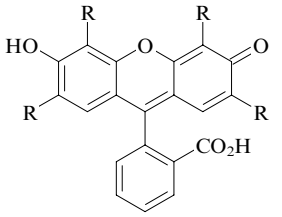
Comprehensive studies of PSCL of chlorophyll and its analogues were carried out by Krasnovsky (Jr) *et al.*[12–17] In a review,[17] the major experimental approaches to investigations of light-created CL have been outlined and, first of all, the process has been proposed to be divided into photochemical and chemiluminescence stages. Studies of the photochemical stage involve the determination of an action spectrum of the exciting light, the elucidation of the role of oxygen in the photoirradiation and the determination of the nature of the primary photoproduct. The use of thermograms of CL ignition in the course of heating of deeply frozen photoirradiated aerated solutions has been pioneered in studies of the chemiluminescence stage. Thermograms reflect the involvement of various labile photoproducts in CL (*i.e.*, in 'photothermochemiluminescence').

The efficiency of chlorophyll PSCL is low, namely, one emitted quantum per 10^8 absorbed quanta. The general scheme of PSCL of chlorophyll (Chl) can be represented as the following reaction sequence:

$$\text{Chl} \xrightarrow{h\nu} {}^1\text{Chl}^* \longrightarrow {}^3\text{Chl}^* \xrightarrow{O_2} (\text{Chl}\cdots{}^1O_2) \longrightarrow$$
$$\longrightarrow \text{Chl}{-}O_2 \xrightarrow{\Delta} Y_1^*, Y_2^*, \ldots \longrightarrow Y_1, Y_2, \ldots + h\nu_1, h\nu_2, \ldots$$

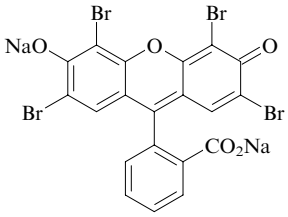
Light quanta are radiated by emitters Y_1, Y_2, ..., *i.e.*, the products of chlorophyll oxidation.

PSCL of aerated solutions of fluorescein (**1**), erythrosine (**2**), eosin Y (**3**), Rose Bengal (**4**), rhodamine B (**5**), safranine (**6**), thionine (**7**), Methylene Blue (**8**), Acridine Orange (**9**), anthracene and naphthacene was discovered and studied,[14,17] as well as of pyrene and benzopyrene.[18]

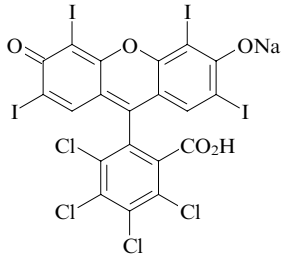


1, **2**

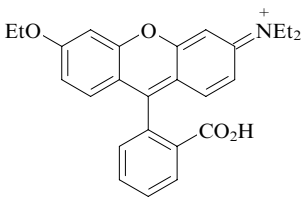
R = H (**1**), I (**2**)



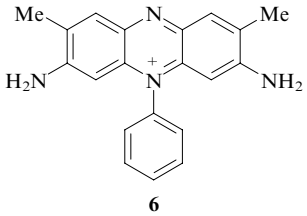
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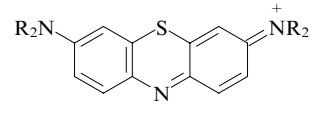
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5

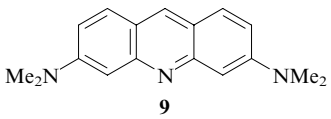


6



7, **8**

R = H (**7**), Me (**8**)



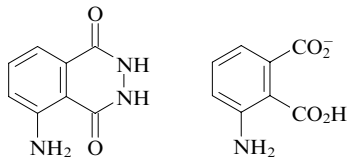
9

The presence of dissolved oxygen at the moment of illumination is a prerequisite for persistent afterglow of the compounds listed. The PSCL yield for solutions of compounds **2**–**4** is maximum in aprotic solvents such as acetone, dioxane, DMF, DMSO. The PSCL spectra differ from the fluorescence spectra of the original compounds. Thus the fluorescence peak of compound **8** is at $\sim$700 nm, while its PSCL peak is at $\sim$560 nm. Based on the studies of the glow decay kinetics and the analysis of photothermochemiluminescence curves, it was concluded that PSCL starts with the formation of several types of labile peroxide compounds.

The observed phenomenon was called [12–17] photochemiluminescence,§ its main feature is photooxidation of the starting compounds in the presence of oxygen.

3. Luminol

In 1961, it was discovered [19] that in aerated solutions containing luminol (5-amino-2,3-dihydrophthalazine-1,4-dione, **10**), a dye (eosin, fluorescein) and a base, chemiluminescence occurs upon irradiation in the region of the dye absorption band. The PSCL spectrum coincided with the CL spectrum of luminol in the presence of an oxidant and corresponded to the fluorescence spectrum of 3-aminophthalate (**11**), *i.e.*, the oxidation product and the CL emitter.



10 **11**

Kuschnir and Kuwana [19] assumed luminol to be oxidised by singlet oxygen, which at that time was considered (and for a good reason) as the driving force of many reaction mechanisms. (It should be noted that Foote's study [20] in which he attributed the photosensitised oxidation of substrates to the electron transfer rather that the action of singlet oxygen was published much later.)

This mechanism was called into question in a study by Matheson and Lee,[21] who, based on the kinetic analysis, ruled out the possibility of direct involvement of singlet oxygen in PSCL. Later, in the determination of the rate constant for the luminol reaction with $^1O_2$ ($\sim 3\times10^7$ litre mol^{-1} s^{-1}), it was shown that the structure of the final product of luminol oxidation with singlet oxygen differed from that of compound **11**. The CL yield in the luminol reaction with singlet oxygen was $< 3\times10^{-9}$ per luminol molecule, which is infinitesimally small as compared with the quantum yield of PSCL.[22]

A detailed study of PSCL of luminol and other phthalohydrazides was carried out by Emokhonov and co-workers.[23–27] They used eosin and Methylene Blue as the photosensitisers. The action spectrum of light for PSCL coincided with the absorption spectra of these dyes. In the UV region, which corresponds to the luminol absorption, autosensitisation occurred, *i.e.*, in the UV illumination, liminol itself served as the photosensitiser. Both photochemiluminescence and autosensitised CL of luminol were quenched by superoxide dismutase. Hence, superoxide ions play an important role in PSCL of luminol. This catalytic cycle (see Table 1, type Ib) includes the following stages:

(1) light absortion by the sensitiser and its transition into the triplet state;

(2) electron transfer from a luminol molecule to the triplet sensitiser to form radicals (or radical ions) of the sensitiser and luminol (under the experimental conditions, *i.e.*, in a phosphate buffer with pH 10–12, luminol, eosin and their radicals exist in the form of anions, while Methylene Blue exists in the form of a cation, and its radical is neutral);

(3) oxidation of the sensitiser radical with dissolved oxygen to afford a superoxide ion and to recover the sensitiser in its original state.

The rate constant for the third stage is 2×10^8 litre mol^{-1} s^{-1} for eosin and 5×10^5 litre mol^{-1} s^{-1} for Methylene Blue. The reaction of the luminol radical with a superoxide ion is the key stage of the luminescence pathway of luminol reaction, its rate constant is $\sim 7\times10^7$ litre mol^{-1} s^{-1}. It was shown that the reaction of luminol with singlet oxygen afforded an unstable product that quenched PSCL. Its lifetime amounts to minutes and seconds when isoluminol and 4-dimethylaminophthalohydrazide are used. This explains the intricate (with two peaks) kinetic curve of PSCL of these compounds. The formation of a quencher complicates the CL kinetics. The side effect could be avoided if the PSCL experiments employed pulsed illumination rather than stationary.[24] Figure 1 *a* shows the kinetics of luminol PSCL initiated by a flash of $\sim$10 μs ($\lambda > 610$ nm) from a flash lamp.

PSCL of luminol induced by radiation from a pulsed laser ($\lambda = 530$ nm) and a stationary source was studied.[28] Figure 1 *b* shows the PSCL spectrum for the laser stimulation. The marked segments correspond to chemiluminescence caused by the involvement of singlet oxygen (type II) and initiated by the electron transfer (type I). A comparison of curves in Figs 1 *a*,*b* shows that they substantially differ, first of all, in the time intervals of the

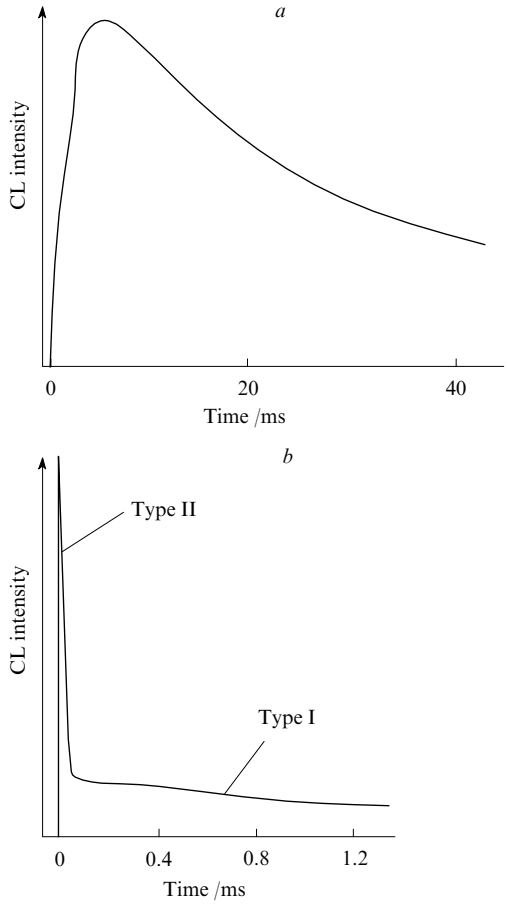


Figure 1. PSCL spectra of luminol with a sensitiser excited by filtered light from a pulse lamp ($\lambda > 610$ nm, CL registration in a band at 380–480 nm) (*a*) and a laser pulse ($\lambda \sim 530$ nm, registration at 420 nm) (*b*).[28]

§ At present, the term 'photochemiluminescence' is understood as a mnemonic code of the sequence of operations with the reaction mixture (or as a protocol of the experiment), *cf.* the use of the term 'photothermochemiluminescence' mentioned above.

PSCL evolution. The assignment of the initial flash to the chemiluminescence induced by the formation of singlet oxygen has not yet been proved. The role of $^1O_2$ in the luminol PSCL might be clarified by the detection of emission in two spectral channels, *viz.*, in the blue region of the luminol CL emission band and at 1270 nm in the emission band of singlet oxygen.

The kinetics of autosensitised CL of luminol upon the pulsed-laser UV irradiation (λ = 347 nm) was studied.[27] It was shown that the primary process corresponds to the one-photon ionisation of luminol to afford a luminol radical and a hydrated electron (e_{aq}). The latter is captured by dissolved oxygen to form a superoxide ion. The subsequent reaction of the luminol radical with the superoxide ion is accompanied by chemiluminescence. Scheme 1 [29–31] shows the mechanism of this process and the structures of reactants and intermediates.

Scheme 1

$LH_2 \rightleftharpoons LH^- + H^+$ (pK_a = 6.3–6.7),

$LH^+ \xrightarrow{h\nu_1} LH^{\bullet} + e_{aq}$,

$LH^{\bullet} \rightleftharpoons L^{-\bullet} + H^+$ (pK_a = 7.7),

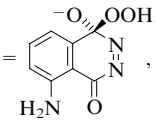
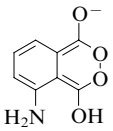
$L^{-\bullet} + O_2^{-\bullet} \longrightarrow LO_2^{2-}$,

$LO_2^{2-} + H^+ \rightleftharpoons LO_2H^-$ ($pK_a \approx 16$),

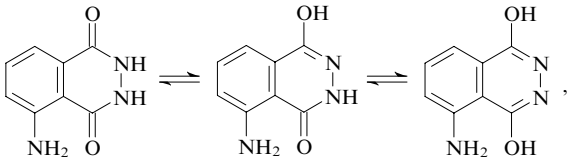
$LO_2H^- \longrightarrow$ **12** + N_2,

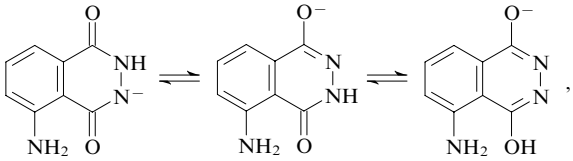
12 $\longrightarrow$ (**11**)*,

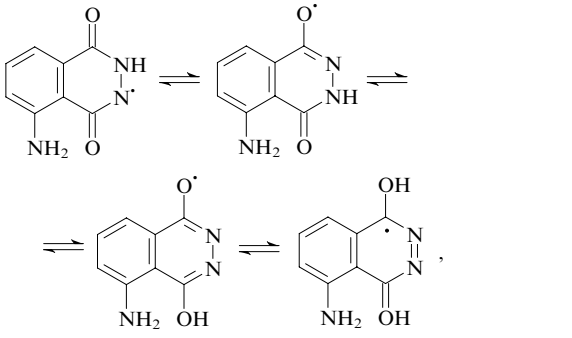
(**11**)* $\longrightarrow h\nu_2$ + **11**.

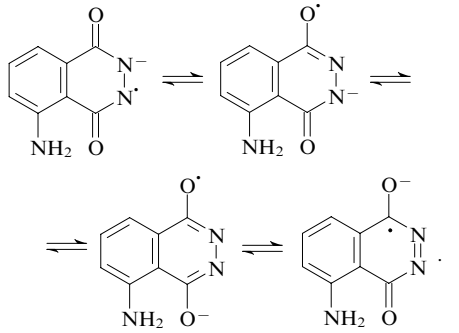
LO_2H^- = , **12** = 

Structures of LH_2 (**10**), LH^-, $LH^{\bullet}$ and $LH^{-\bullet}$ can be presented as tautomeric equilibrium forms (1)–(4), respectively,


(1)


(2)


(3)


(4)

To explain the PSCL of luminol, a general scheme of photosensitised oxidation according to which luminol is the oxidised substrate was used.[32] From our viewpoint, the new name of this phenomenon, 'optically pumped chemiluminescence', offers less information.

Although the nature of luminol PSCL long remained unclear, this phenomenon was already used in the medical and biological studies of antioxidants.[33–39] Certain progress was achieved in the application of PSCL for the analysis of antioxidant activity of substances; however, the applicability of PSCL for these purposes has recently been questioned because of the absence of any correlation in the activity estimates made using PSCL and other methods.[40] It is the fact that in luminol PSCL the main targets of antioxidants are luminol radicals and superoxide ions that probably accounts for the lack of correlation.

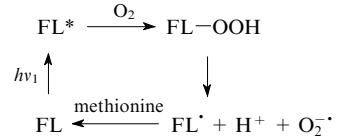
Photosensitised chemiluminescence of luminol was also proposed [32] to be used for the detection of antibodies covalently stained with Methylene Blue (up to 16 photosensitiser molecules per antibody); based on this reaction, a method of immunochemical assay of α-fetoprotein has been developed (detection limit 1.7×10^{-11} g).

4. Lucigenin and analogues of luciferin

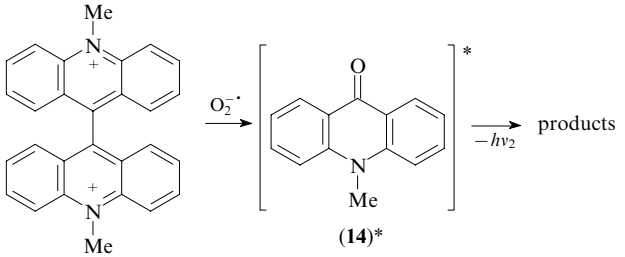
Lucigenin (*N*,*N*′-dimethylbiacridylium ion, **13**), like luminol, is a widely known chemiluminophore the oxidation of which is accompanied by bright CL.

Riboflavin-photosensitised chemiluminescence of lucigenin was studied.[41,42] UV irradiation of riboflavin generates superoxide radical ions the reaction of which with lucigenin leads to excited *N*-methylacridone (**14**), which is the chemiluminescence emitter (Scheme 2). This mechanism is confirmed by the fact that the addition of superoxide dismutase into the reaction mixture quenches the glow. The addition of methionine into the reactor is aimed at reduction of riboflavin radicals.

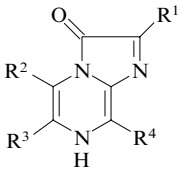
Scheme 2



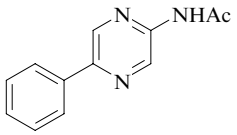
FL is riboflavin.



In the 1980s, chemiluminophores **15**, which represent the analogues of luciferin (coelenterazine) inducing the glow of certain medusas and *Cypridina* hermit crabs, were synthesised (see Ref. 43 and references cited therein).



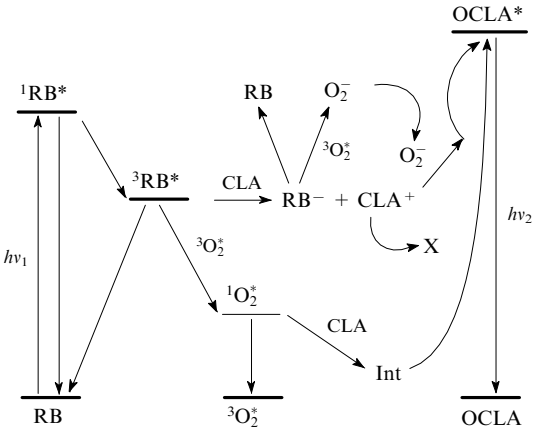
15



16

One of the analogues, *viz*., 2-methyl-6-phenyl-3,7-dihydroimidazo[1,2-*a*]pyrazinone (**15**, $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = Ph$) was named CLA (Cypridina Luciferin Analogue). The CLA chemiluminescence photosensitised by Rose Bengal (RB) in an aqueous solution with pH 7 was studied.[44] The reaction proceeds through the formation of excited 2-acetamido-5-phenylpyrazine (OCLA, **16**), which is the CL emitter, and of an unidentified intermediate (Int), which is the reaction product of CLA with singlet oxygen (Scheme 3).

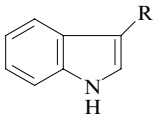
Scheme 3



Photosensitised oxidation of CLA includes the same stages as the luminol oxidation; however, the intermediate formed in the CLA reaction with $^1O_2$ also takes part in the luminescence transformations.

5. Indole derivatives

Photosensitised chemiluminescence of indole (**17a**) derivatives was discovered following observation of persistent afterglow of proteins and amino acids[45,46] and of solutions of proteins and synthetic polymers irradiated with X-rays[47] and UV light.[48]



17a–d

R = H (**a**), $CH_2CH(NH_2)CO_2H$ (**b**),

$CH_2CH(NHCOCH_2NH_2)CO_2H$ (**c**), CH_2CO_2H (**d**).

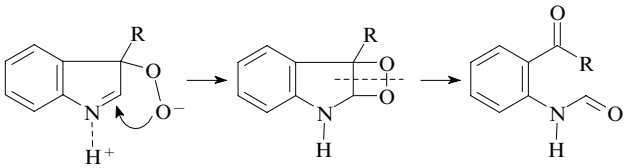
In 1968, Sapezhinskii and Voloshin[49] reported on chemiluminescence accompanying the photooxidation of tryptophan (**17b**) in aerated solutions. Later, this research group studied the autosensitised CL of glycyltryptophan (**17c**) and its dye-sensitised chemiluminescence.[50–58] The results of studies of radiation-induced CL in peptides, proteins and synthetic polymers were generalised in a monograph.[59]

The photoexcitation site of a sensitiser can be fixed by its adsorption on a plate immersed in the substrate solution.[55] The idea of spatial separation of a sensitiser and a solution exposed to sensitisation products was forwarded in the studies of photosensitised oxidation[5] and PSCL of glycyltryptophan.[55] This heretogeneous PSCL offers good prospects in analytical applications and in the development of chemiluminescence sensors.

The phenomenon of autosensitised CL of tryptophan (**17b**) upon its UV irradiation was studied by several optical techniques.[60] CL in the blue region was attributed to tryptophan photooxidation. Chemiluminescence at 630–705 nm was intensified in heavy water and quenched by 10%–15% upon the addition of NaN_3 and DABCO. This suggests that dimolar luminescence of singlet oxygen made a certain contribution to the total CL

$$^1O_2 + {}^1O_2 \longrightarrow [^1O_2 \cdots {}^1O_2]? \longrightarrow 2\,O_2 + h\nu.$$

Rose Bengal-photosensitised CL of indol-3-ylacetic acid (**17d**) was studied.[61] Superoxide ions and singlet oxygen were the major photooxidants of indole derivatives. The attachment of superoxide at position 3 of the indole molecule was accompanied by the formation of intermediate dioxetane; cleavage of C–C and O–O bonds in the latter led to formylkynurenine derivatives (**18a–d**).



17a–d **18a–d**

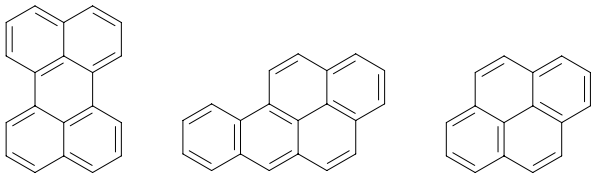
Opening of the dioxethane ring was accompanied by the release of energy >270 kJ mol^{-1}, which is quite sufficient for the chemiexcitation of the carbonyl product.[60] The formation of dioxetane intermediates is probably typical of all indole derivatives.[62]

The phenomenon of PSCL of glycyltryptophan (**17c**) was used in the determination of the activity of superoxide dismutase in its reaction with riboflavin as the photosensitiser and for studying the photoprotection and antioxidant properties of a series of natural compounds and medicinal drugs.[63–70]

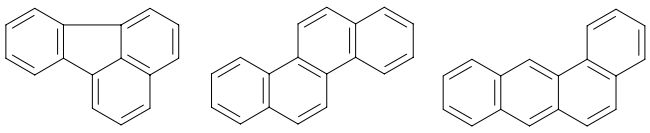
Yet another application field of the PSCL of indole derivatives are the studies of conformational transformations of proteins induced by various effects.[71–73] Insofar as most proteins contain tryptophan, the intensity of protein PSCL depends on the number of tryptophan residues accessible for photooxidation.

6. Polyaromatic hydrocarbons

PSCL of aerated solutions of anthracene, naphthacene, pyrene and benzopyrene as well as base-induced enhancement of glow was first reported in the 1970s.[17,18] Chemiluminescence appeared upon mixing of a solution of an organic base (triethylamine, piperidine) with aerated and irradiated (λ > 320 nm) solutions of polyaromatic hydrocarbons (PAH) in CCl_4, acetone or benzene.[74] The highest CL yield was observed in CCl_4 solutions of the following PAH (the series is given in order of decreasing CL quantum yield): perylene (**19**), benzo(*a*)pyrene (**20**), pyrene (**21**), fluoranthene (**22**), chrysene (**23**), 1,2-benzanthracene (**24**), 9,10-diphenylanthracene, anthracene.



19 **20** **21**



22 **23** **24**

Presumably, UV irradiation of PAH solutions results in the photoionisation of the substrate to form the corresponding radical cation and a photoelectron, which is captured by the solvent.[74] Subsequent interaction of PAH radical cations with dissolved oxygen leads to the formation of, first, peroxide radicals and, then, peroxides. Chemiluminescence is induced in the reaction of primary and secondary peroxides with hydroxyl anions HO^- or a base. The proposed mechanism brings about many questions. For example, is it possible to distinguish light-generated radical cations from those formed as a result of electron transfer from an excited PAH molecule to oxygen, based on observations of radical cations alone? Apparently, the insight into the mechanism requires additional studies.

PSCL of fluoranthene (**22**)[74] can be compared with studies[75] of base-induced CL reactions of this compound. It is reasonable to assume that the chemiluminescence of compound **22** and other PAH, which was observed in Ref. 75, was, in fact, PSCL initiated by the laboratory light.¶

7. Chromone-2-carboxylic acid

The primary process of the reaction of a light-excited molecule with oxygen can be not only the transfer of an electron or excitation energy to the oxygen molecule to form $^1O_2$, but also the addition of oxygen to the substrate molecule (type II c photooxidation, see Table 1). Thus in studies[76,77] devoted to PSCL of aerated solutions of chromone-2-carboxylic acid (**25**), it was shown that its photolysis affords 4-hydroxycoumarin (**26**) as the only product, which corresponds to the formal substitution of oxygen for the carboxyl group in the starting molecule. Compound **26** is not formed in either deoxygenated or aerated solutions in the presence of sensitisers (Methylene Blue and Rose Bengal). It was thus concluded that it is the ground-state oxygen molecule rather than its active form that takes part in the reaction. Moreover, the photolysis of compound **25** was not accompanied by the formation of ketyl radicals, typical products of the abstraction of hydrogen atoms from solvent molecules by excited ketones. The presence of a strong electron-withdrawing group in the molecule of keto acid **25** makes the electron transfer from the excited molecule **25** to the O_2 molecule impossible. Hence, the primary process of photolysis consists of the addition of oxygen to the excited molecule of coumarin **25** the triplet state ($n\pi$-type) of which has the structure of biradical **27** (Scheme 4).

Chemiluminescence (hv_2) of irradiated solutions of compound **25** arises due to the reactions of peroxide radicals **28**. Exponential decay of CL intensity following the irradiation of solutions was observed with a rate constant of 4.2×10^{-4} s^{-1}. Unfortunately, Scheme 4 does not explain this peculiarity of the kinetics. Moreover, disproportionation of tertiary peroxide radicals does not lead to product **26**, being only the source of hydroxyl radicals, and cannot be assigned to chemiexcitation reactions.[78–80] It should be noted that the possibility of photoionisation of acid **25** cannot be totally ruled out, because this was observed for certain derivatives of 4-oxoquinoline-3-carboxylic acid.[81]

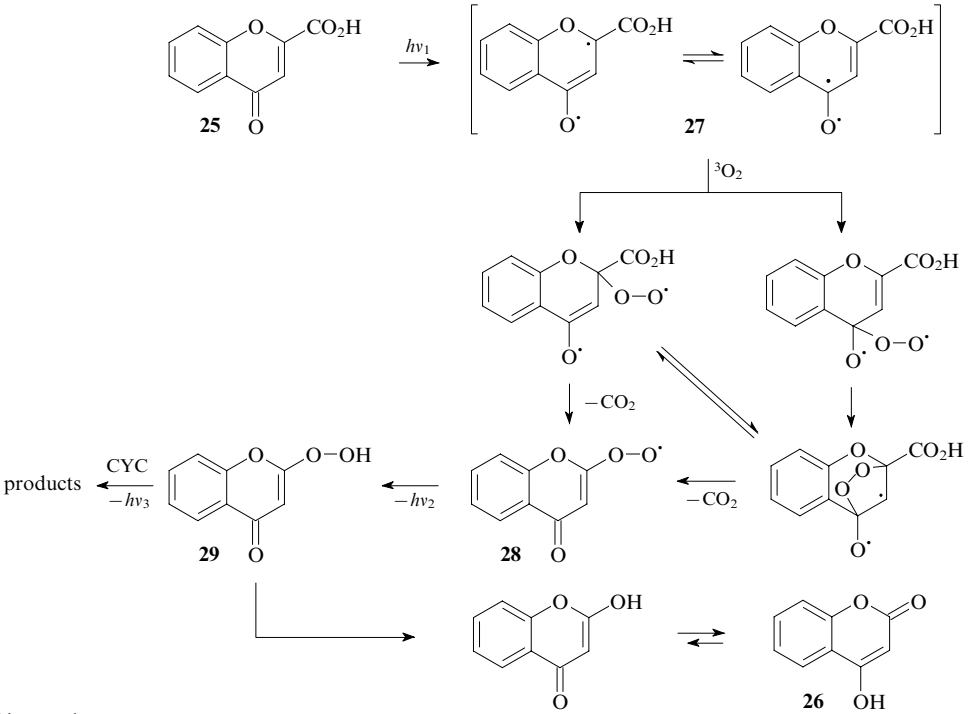
Chemiluminescence (hv_3) also arises when an iron-containing protein, namely, cytochrome *c*, which catalyses decomposition of hydroperoxides, is added to a photosensitised ethanolic solution of compound **25**.[77] This enhances the emission intensity 30-fold as compared with the CL intensity observed immediately after the irradiation. This can be considered as evidence for the formation of hydroperoxide **29** in the photolysed solution (see Scheme 4). However, this process calls for further investigations.

8. Organic azides

Zelentsov and co-workers[82,83] observed chemiluminescence in the oxidation of organic azides with molecular oxygen in ethanol under UV irradiation ($\lambda > 280$ nm), where the CL spectrum of photooxidation of 4,4′-diazidobiphenyl had two peaks in the blue region. Presumably, the chemiexcitation occurs in the isomer-

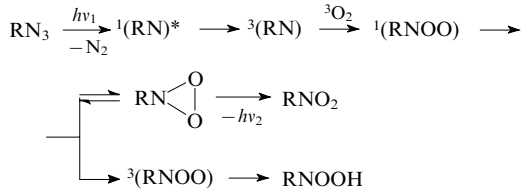
¶ Berger *et al.*[75] ignored the possibility of phototransformation of reagents at the stage of solution preparation and pretreatment; this is why they assigned this reaction to CL.

Scheme 4



CYC is cytochrome *c*.

isation of dioxaziridine (a dioxirane analogue) to afford a nitro compound with energy release (>315 kJ mol^{-1}).



R = Alk, Ar.

Apparently, the nitro compound serves as the emitter.

In 1954, when studying the luminescence of nitro-substituted biphenyl and stilbene, Lippert [84] observed no fluorescence in the region <500 nm. However, the shift of the absorption band of a nitro compound to the long-wave region (by varying solvents or substituents in the nitro compound) gave rise to fluorescence at $\lambda > 500$ nm. Thus, nitro compounds with peaks of long-wave absorption bands below 500 nm do not fluoresce (the so-called Lippert rule),[85] *i.e.*, nitro derivatives do not exhibit blue luminescence.

The question of the nature of the emitter could be solved ultimately using an organic azide the photooxidation product of which exhibited known luminescence properties. Thus for 4-azido-4′-dimethylaminostilbene, the presumed emitter would be 4-dimethylamino-4′-nitrostilbene which emits with the quantum yield of 0.7 luminesces at 590 nm.[86]

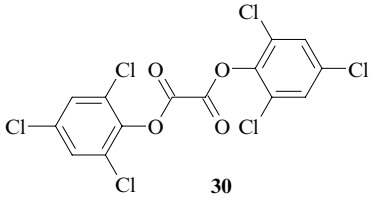
9. Complex systems

In a photolysed solution that originally contained a single substance, a complex mixture of different products and intermediates is gradually formed. Moreover, if the solution to be photolysed originally contained a mixture of substances, the elucidation of the mechanism of phototransformations becomes an extremely difficult task. Nonetheless, the PSCL phenomenon was described for complex systems too.

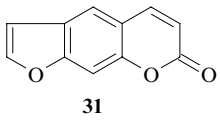
PSCL of certain high-boiling oil fractions was observed.[87] Aerated samples (at 77 K) were irradiated in different spectral ranges for different exposure times. Emission was registered in the course of sample heating from 77 to 550 K. Several temperature zones in which light was emitted in a range of 400 – 700 nm with peaks at 520 – 550 nm were revealed.

PSCL of aerated aqueous solutions of humic acids, both natural and synthetic, was studied.[88,89] A relationship was established between the observed CL and the photooxidation process, CL and fluorescence spectra were recorded and their changes with the photolysis time were revealed. Presumably, the photodecomposition products are the CL emitters in this process; moreover, the energy is transferred from primarily excited species to chromophores in the polymer, which become the emitters of light.

PSCL of bis(2,4,6-trichlorophenyl) oxalate (**30**) observed upon mixing of its photolysed aerated solution in isopropyl alcohol with an unirradiated solution of anthracene (or some other polyaromatic fluorophore) was described.[90] It should be noted that a mixture of diaryl oxalates with fluorophores enters into the composition of commercial light sources in which the glow is 'triggered' by the addition of H_2O_2 solutions. However, in this case, the PSCL effect is caused by reasons other than the photosynthetic formation of hydrogen peroxide.



30



31

Chemiluminescence that arises upon mixing of a UV-photolysed aerated solution of psoralene (**31**) with a solution of $FeSO_4$ in a Tris buffer (pH 7.4) was described;[91] however, the mechanism of this phenomenon was not considered in detail.

In closing this Section, it should be noted that characteristic feature of photosensitised chemiluminescence is the photooxidation in the presence of molecular oxygen, chemical transformations of the reaction products being accompanied by chemiluminescence.

III. Photochemical synthesis of chemiluminescent reagents

In the definition of light-created chemiluminescence systems given in the Introduction, attention was paid only to the order in which the stages of illumination and CL observation occur. The time factor (*i.e.*, the interval between these stages) was ignored. In the PSCL processes discussed above, the chemiluminophores formed, *viz.*, hydroperoxides and 1,2-dioxetanes, were characterised by relatively short lifetimes. However, sufficiently stable chemiluminophores are known to be formed photochemically. These can be both peroxides (particularly, 1,2-dioxetanes) and other classes of chemical compounds. The photochemical method can also afford reactants that, being added to solutions of chemiluminophores, induce chemiluminescence.

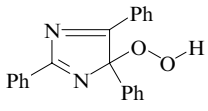
1. Chemiluminophores obtained by photochemical methods

a. Lophine peroxide

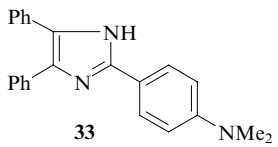
Lophine hydroperoxide (4-hydroperoxy-2,4,5-triphenylimidazole, **32**) was synthesised in 1964 upon illumination of a lophine solution in chloroform (18 °C) in the presence of Methylene Blue and oxygen in 68% yield.[92]

It was assumed earlier [93] that this compound is an intermediate in the chemiluminescence reaction of lophine with oxygen in an alkaline medium. It was proved that the reaction product is hydroperoxide rather than lophine endoperoxide. Chemiluminescence of peroxide **32** was observed in the thermolysis ($T > 110$ °C) and also under the action of bases in the absence of oxidants.

An unusual effect of light on a chemiluminescence system was observed.[94] Gradual decay of chemiluminescence during the oxidation of 2-(*p*-dimethylaminophenyl)-4,5-diphenylimidazole (**33**) with molecular oxygen was observed; however, the illumination of the partly reacted mixture restored the glow up to its original level.



32



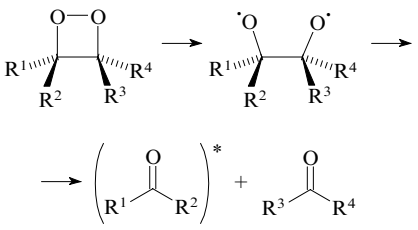
33

According to one of explanations of this effect, the dark transformation pathway of compound **33** involves the formation of an inactive dimer, which decomposes in the light to the starting inidazole and its peroxide derivative.

b. 1,2-Dioxetanes

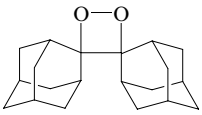
1,2-Dioxethanes are four-membered cyclic peroxides, which attract great interest as chemiluminophores. Chemistry, mechanisms and applications of CL of these compounds are documented in surveys [43,95,96] and books.[97,98]

Unimolecular decomposition of 1,2-dioxethane into two carbonyl compounds proceeds *via* a biradical and is accompanied by liberation of energy of about 290 kJ mol^{-1}. This energy (even ignoring the activation energy) is sufficient for the excitation of one of the products.



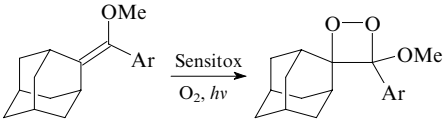
$R^1 - R^4$ = Alk.

The addition of photochemically generated singlet oxygen to the C=C bond of a precursor molecule is a convenient method for the synthesis of 1,2-dioxethanes.[99–107] It is this method that was used in the synthesis of the first dioxetane (**34**)[99,100] stable under normal conditions from adamantylideneadamantane. Its yield depended on the sensitiser and solvent used. Improper combination of the latter resulted in a dramatic increase in the yield of side epoxide.[101] Other limitations for the photochemical synthesis of 1,2-dioxethanes are also known.[107]



34

Photooxygenation of alkene **35** in CH_2Cl_2 employed polymer-bound Rose Bengal (Sensitox),[102] which facilitated the separation of the sensitiser from the product. Irradiation of the solution (15–30 min), removal of the sensitiser and evaporation of the solvent afforded the product, dioxetane **36**.



35 **36**

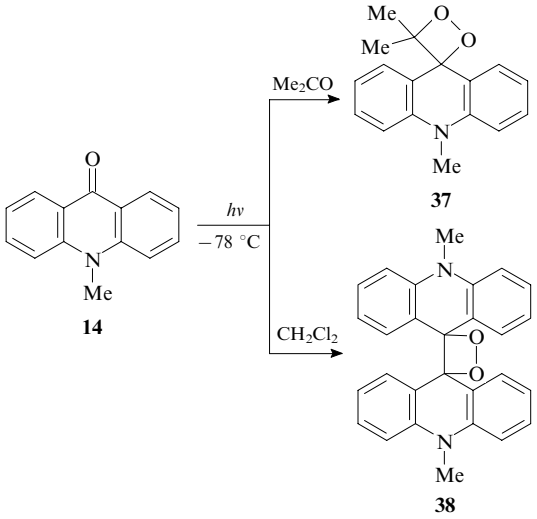
The earlier version of this reaction employed a heterogeneous photogenerator of singlet oxygen.[103]

The kinetic stability of dioxetane **36** under normal conditions is due to the high activation barrier to its decomposition. Thermolysis of this compound is accompanied by CL. Chemical excitation of dioxetane **36** is characterised by a high (up to 60%!) yield of triplet carbonyl compounds. The yield of products in the excited singlet state is lower by a factor of 10–1000. Efficient population of the triplet term is attributed to the fact that, according to the Hund rule, this is the lower term in the intermediate biradical (the transition state in the decomposition).[80]

The presence of electron-donating groups in the dioxetane molecule favours partial population of the antibonding π*-orbital of the O–O bond. This dramatically decreases the activation barrier to decomposition so that this can begin even at ambient temperature. The decomposition process can be controlled by introducing an electron-withdrawing group into the composition of the aromatic substituent of compound **36**. The interaction of this group with a special reagent (trigger) resulted in the transformation of the starting molecule into *m*-methoxycarbonylphenolate anion, partial electron transfer to the π*-orbital of the O–O bond and decomposition of the dioxetane (Scheme 5, pathway *a*).

The thermal (pathway *b*) and the electron-transfer-initiated mechanisms of decomposition of compound **36** were studied.[108,109] It was found that in the thermal process, the triplet states $^3(n\pi^*)$ of adamantan-2-one and $^3(\pi\pi^*)$ of methyl *m*-alkoxybenzoate are excited in similar quantum yields (~0.1) and the singlet state $^1(n\pi^*)$ of adamantan-2-one is excited in an insignificant yield. In the electron-transfer-initiated decomposition of dioxetane, only the singlet state $^1(\pi\pi^*)$ of the corresponding phenolate anion is excited. Such a striking difference points to the fundamental difference in the mechanisms of the decomposition and chemical excitation in the thermolysis, on the one hand, and the process initiated by the electron transfer, on the other hand (see Scheme 5).

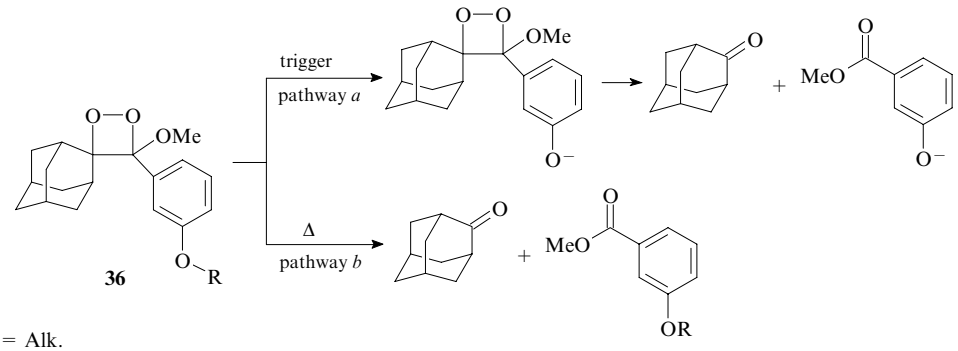
The photochemical synthesis of 1,2-dioxetane can be carried out by a different route, namely, by the total reversal of the chemical excitation process. Irradiation of an acetone solution of *N*-methylacridone (**14**) with light from a high-pressure mercury lamp in an argon atmosphere at −78 °C afforded a cycloaddition product, 1,2-dioxetane **37**,[110] while irradiation of a solution of compound **14** in CH_2Cl_2 under the same conditions led to 1,2-dioxetane **38**.



14 **37** **38**

Thermolysis of dioxetane **37** gave rise to CL the spectrum of which coincided with the fluorescence spectrum of compound **14** in acetone (λ_{max} = 525 nm), the CL quantum yield reached 10^{-6}. Unfortunately, the preliminary communication[110] was not followed by more detailed investigations. At the same time, it is

Scheme 5



36

R = Alk.

known that *N*-methylacridone (**14**) exhibits ππ*-phosphorescence with a well resolved vibrational structure.[85] Hence, is would be interesting to obtain its complete CL spectrum.

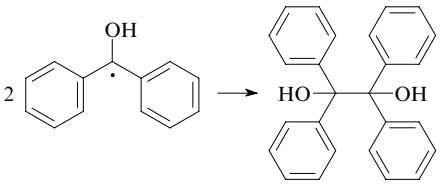
Photochemical synthesis of dioxetanes has found its application not only in preparative chemistry, but also in the on-line kinetic analysis of samples.[111]

c. Pinacols

UV irradiation ($\lambda > 320$ nm) of an acetone solution of acridone **14** in an argon atmosphere at room temperature (*i.e.*, under the conditions where dioxetanes **37** and **38** decompose) affords products that require the combined action of an oxidant (*e.g.*, oxygen) and a strong base for their chemiluminescence to be initiated.[74] These products are pinacols (1,2-glycols).

The synthesis of different chemiluminophores under UV irradiation of the corresponding carbonyl-containing polyaromatic hydrocarbons was described.[74] The similarity of conditions of the photochemical treatment of these compounds did not guarantee the formation of the same chemical class of products: the starting substances belong to substantially different spectral-luminescent classes and, hence, possess different photochemical properties.

Pinacols are the products of photoreduction of many aromatic carbonyl compounds. For example, dimerisation of radical products of benzophenone photoreduction yields benzopinacol (**39**).

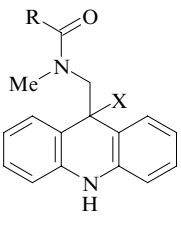


39

The dimerisation constant of neutral ketyl radicals is $10^{10}-10^{13}$ litre mol^{-1}. Just as each dioxetane molecule can be said to 'harbour a photon',[97] each molecule of certain pinacols can be said to contain two radicals. This is explained by the fact that in strongly alkaline media pinacols lose their stability and undergo dismutation *via* ketyl radicals and radical anions.[112] The radical processes are frequently accompanied by chemiluminescence. The acidity of pinacols ($pK_a \approx 14$) is substantially lower as compared with ketyl radicals;[113] hence, initiation of radical reactions involving pinacols requires a strongly alkaline medium. It is assumed that photochemically generated pinacols play the role of important intermediates in the chemiluminescence of photolysed solutions of aromatic carbonyl compounds. In the presence of oxidants, pinacols can become dioxetane precursors.

d. Acridans

The first members of a new family of chemiluminescent reactants, namely, dihydroacridines (acridans) **40a**, were prepared by the photolysis of deaerated solutions of acridine in DMF (for R = H) or dimethylacetamide (for R = Me).[114] In solutions of acridans **40a**, the quantum yield of chemiluminescence initiated by strong bases (NaH, Bu^{t}OK, MeONa) in the presence of O_2 reaches 0.006.



40a–c

R = H, Me; X = H (**a**), OH (**b**), CH_2Ph (**c**).

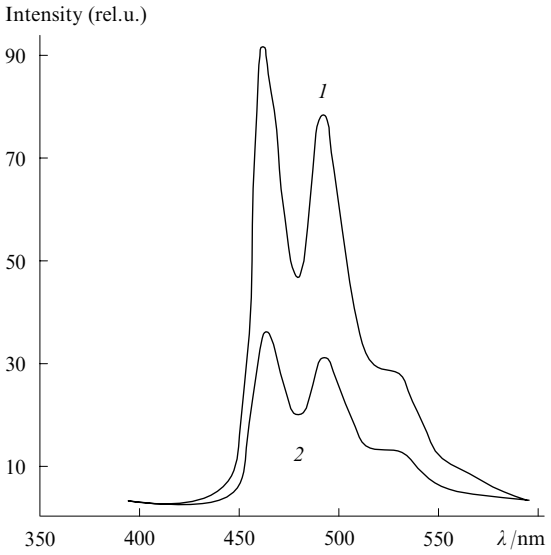
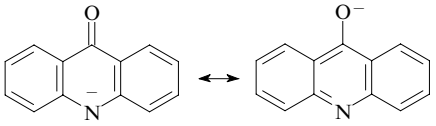


Figure 2. Fluorescence spectrum of anion **41** (*1*) and CL spectrum of compound **40a** (*2*).

The acridone anion (**41**) is the emitter of radiation. Figure 2 shows the CL spectrum of compound **40a** (curve *2*) and the fluorescence spectrum of anion **41** (curve *1*), which have similar patterns.



41

γ-Radiolysis produces[115] acridans **40b**,**c** and their *N*-methyl derivatives. The quantum yield of CL of acridans **40b** (R = H or Me) exceeds 0.01.

It is known that oxidation of 9-methylacridine with molecular oxygen in DMF in the presence of Bu^{t}OK is accompanied by chemiluminescence.[116] Here, acridone anion served as the emitter. This brings up the question: would this be a chemiluminescence reaction if solutions of 9-methylacridine were prepared in darkness thus excluding the possibility of chemiluminophore photogeneration?

e. Ruthenium complexes

The bipyridyl complex of Ru(III) is a bright example of chemiluminophores based on metal complexes.[117–119]

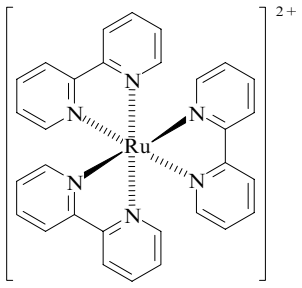
Chemical excitation of ruthenium cation occurs in the reaction of Ru(III) bipyridyl complex with a reducing agent (Red) with the standard redox potential < 0.86 V.

$$Ru(bipy)_3^{3+} \xrightarrow{Red} \left[Ru(bipy)_3^{2+}\right]^* \xrightarrow[-h\nu]{} Ru(bipy)_3^{2+}$$

bipy is 2,2 -bipyridyl.

Complex $Ru(bipy)_3^{2+}$ (**42**) is sufficiently stable (it withstands boiling in concentrated HCl or 50% NaOH solutions) and chemically inert, whereas $Ru(bipy)_3^{3+}$ is chemically reactive.[119]

For the chemiluminescence analysis, $Ru(bipy)_3^{3+}$ was synthesised from cation **42** by different methods,[120] *e.g.*, by the photochemical activation of $Ru(bipy)_3^{2+}$ oxidation with peroxydisulfate ions.[121] Optical absorption of the $[Ru(bipy)_3^{2+}]$ complex at the 450 nm band ($\varepsilon = 14\,600$) results in the populationin, with the quantum yield equal to 1, of the excited state $[Ru(bipy)_3^{2+}]^*$



42

(lifetime ~ 0.6 μs). In the excited state, the complex acquires reductive properties and is oxidised by the $S_2O_8^{2-}$ ion.

$$[Ru(bipy)_3^{2+}]^* + S_2O_8^{2-} \longrightarrow Ru(bipy)_3^{3+} + SO_4^{2-} + SO_4^{-}$$

The SO_4^- ion formed oxidises the ground-state $Ru(bipy)_3^{2+}$ complex.

$$Ru(bipy)_3^{2+} + SO_4^{-} \longrightarrow Ru(bipy)_3^{3+} + SO_4^{2-}.$$

As a result, the quantum yield of the formation of $Ru(bipy)_3^{3+}$ complex is equal to 2.

A flow photochemical synthesis of $Ru(bipy)_3^{3+}$ ions was used for the chemiluminescence detection of certain compounds.[122–124] It those cases where the compound to be analysed was a weak reducing agent, it was proposed to subject it to photochemical decomposition into the fragments capable of reducing the metal ion in the metal-complex chemiluminophore, thus triggering the CL.[125]

2. Photoactivation of substrates

Illumination of solutions containing chemiluminescent substrates and an oxidant in the spectral region of the oxidant absorption band results in the formation of active forms of the oxidant, which are capable of exciting the CL of an appropriate chemiluminophore. Thus mixing of a UV-irradiated solution of potassium nitrate with an unirradiated solution of luminol induced excitation of chemiluminescence of luminol.[126] The nitrate ion has two absorption bands in the UV range at 202 ($\varepsilon = 9500$) and 304 nm ($\varepsilon = 7$). Chemiluminescence of luminol arises only upon irradiation of the nitrate solution in the region of the first absorption band. The luminol oxidation and the excitation of its CL were attributed to the action of peroxynitrite ($ONOO^-$), which is formed from nitrate (NO_3^-) as a result of intramolecular rearrangement upon excitation. In contrast to nitrate, peroxynitrite is a strong oxidant capable of initiating the chemiluminescence oxidation of luminol.[127–130] The resulting photochemically produced peroxynitrite is a structural isomer of the original anion. The reverse reaction [131] will be discussed in the next Section.

The chemiluminescence reaction of luminol with a photoactivated reactant was used for the determination of nitrates in water.[126, 132] Complex chemiluminescence reactions of photoactivated ClO_2 and SO_2 molecules in a mixture of perchloric and sulfuric acids were also described.[133]

* * *

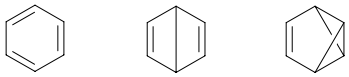
Coupling the procedures of the photochemical synthesis of chemiluminophores and their observation would provide a 'complete' system in which the external effect of light on the reaction mixture gives rise to chemiluminescence. Hence, the above-described examples of the preparation of lophin peroxide from lophin and of dioxetane from alkene in the presence of sensitisers and dissolved oxygen may be considered in the Section devoted to PSCL. However, this is not true for those cases where either the illumination stage requires the use of deoxygenated solutions or the reactions occur independently of the presence of oxygen. The primary photoprocesses (in addition to photooxidation) can include photoreduction, photoaddition and photoisomerisation, which substantially increase the number of photochemical processes that occur in light-created chemiluminescence systems.

IV. Photoinduced chemiluminescence

In the periods of energy crises, the idea of using solar energy gains a new impetus. Active studies on both the conversion of solar energy into electricity and the storage of solar energy as the internal energy of photochemical reaction products, *i.e.*, H_2O_2 (Ref. 134) or structural isomers of different compounds,[135] are initiated. Studies in the latter field have also stimulated the investigation of the reverse process, *viz.*, the conversion of the internal energy of photoproducts into electronic excitation and further into light emission.

1. Photoisomers

The structural formula of a C_6H_6 molecule can be represented as three valence (or structural) isomers, namely, benzene (**43**), Dewar benzene (**44**) and benzvalene (**45**). Structures **44** and **45** were detected in the phototransformation products of isomer **43**.



43 **44** **45**

The enthalpy of formation of structure **44** exceeds that of benzene by 251 kJ mol^{-1}. The isomerisation reaction **44** → **43** has an activation energy of ~ 96 kJ mol^{-1}; hence, ~ 347 kJ mol^{-1} is liberated in the elementary act of molecule rearrangement. This is comparable with the energy of the triplet state of structure **43** (355 kJ mol^{-1}) but smaller than the energy of its excited singlet state (481 kJ mol^{-1}). One can expect such isomerisation to be accompanied by chemical excitation of benzene into the triplet state (^{3}**43**). This process was studied.[136] Insofar as under experimental conditions (solution at ambient temperature) state ^{3}**43** is non-radiative, its detection involves the use of the triplet–singlet transfer of energy from species ^{3}**43** to the singlet fluorophore, namely, 9,10-dibromoanthracene (DBA), with the energy of 310 kJ mol^{-1}. Such a transfer of energy is spin forbidden; however, this prohibition is lifted due to the presence of a heavy atom (Br). The triplet–singlet transfer of energy to DBA is fairly efficient. The reaction **44** → **43**, which occurs on heating of a solution in the presence of DBA is accompanied by chemiluminescence with the spectrum typical of DBA fluorescence. The efficiency of chemical excitation in the reaction **44** → ^{3}**43** is $\sim 2 \times 10^{-4}$; in the case of 1,4-dichlorobenzene, it is equal to $\sim 10^{-3}$.

Thus, it was discovered [136] that the energy stored in a molecule can be converted into the energy of electronic excitation and, under suitable conditions, into light emission. Later, this was demonstrated by the example of thermal isomerisation of Dewar acetophenone,[137] 3,3′-bis(cyclopropenyl) and Dewar xylenes.[138]

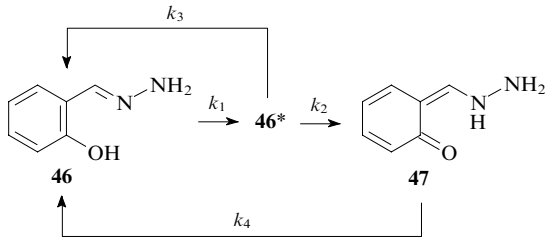
Reaction **45** → **43** is not accompanied by CL,[139] although its elementary act liberates more energy than the isomerisation **44** → **43** discussed above. In the former case, the total energy is converted into heat. This is caused by the great difference in the configurations of structures ^{3}**43** and **45**. In the reaction **45** → **43**, the nuclei in the molecular core should travel considerable distances, which is accompanied by excitation of vibrational modes and dissipation of energy. For **44** → **43**, the configurations of species **44** and ^{3}**43** are virtually identical ('gable roof'), hence, the core restructuring is minimum.

As was already mentioned (see Section III.2), peroxynitrite can be considered as a photoisomer of nitrate. It was shown [131] that spontaneous isomerisation of peroxynitrite to nitrate is accompanied by CL with a quantum yield of $\sim 10^{-9}$. In this case, the quantum yield of chemical excitation of the emitter (peroxynitrite) reaches a very high value (0.2).

$$ONOO^- \longrightarrow NO_3^- + h\nu$$

Structural isomerisation also occurs upon the intramolecular phototransfer of a proton or a hydrogen atom. In this case, the stored energy is small; however, if the reactivity of the isomer formed substantially exceeds that of the original isomer, the former can undergo reactions hindered for the original reactant.

It was shown[140] that chemiluminescence appears in the reaction of salicylaldehyde hydrazone (**46**) with a base if the aqueous solution of hydrazone **46** was pre-irradiated with visible light (400 – 540 nm) with an intensity of merely several milliwatt per square metre. The illumination results in isomerisation of inactive benzenoid form **46** into active quinonoid form **47**. The kinetic scheme of photoinduced formation of isomer **47** can be presented as follows:

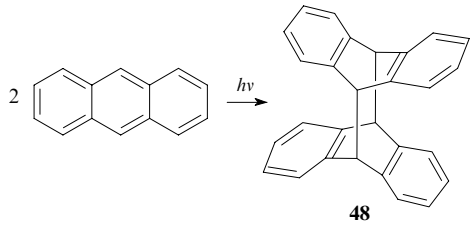


Here, k_1 is the formal constant of photoexcitation of hydrazone **46**, which is proportional to the light intensity (the optical density of solutions is far below 1); k_2 is the rate constant for the transformation of the excited molecule **46*** into the product; k_3 is the rate constant that takes into account all possible processes of degradation of the excited state **46*** that do not lead to compound **47**; k_4 is the rate constant for reaction **47** → **46** [at ambient temperature, $k_4 = (6 \pm 3) \times 10^{-4}$ s^{-1}]. The height of the energy barrier for the transition **47** → **46** is 18 kJ mol^{-1}. In the stationary illumination, the concentration of isomer **47** gradually reached a steady-state value, which is independent of the light intensity and temperature and increases upon the substitution of D_2O for H_2O.

Reactions of a base with both isomers (**46** and **47**) are exothermic and their final product is, probably, the hydrazone anion. However, the enthalpy of formation of isomer **47** exceeds that of isomer **46** by 130 kJ mol^{-1}; hence, the liberated energy is sufficient for the excitation of the reaction product of the base with the former isomer and too low for the latter isomer. This is why chemiluminescence accompanies only the reaction of the base with compound **47** and is not observed in the reaction with hydrazone **46**.

2. Photodimers

Photodimerisation of anthracene is the first photochemical reaction studied. In 1867, Fritsche observed the formation of an unsoluble substance 'paraphoten' (sited according to Ref. 141), *i.e.*, dimer **48**, in a sunlight-exposed benzene solution of anthracene. Its melting produced anthracene.



As was found later,[135] this reaction involves accumulation of energy.

Synthesis of various cyclodimers of anthracene and benzene, particularly, [4π + 4π] heterodimer **49**, was described and their transformations were studied.[142, 143]

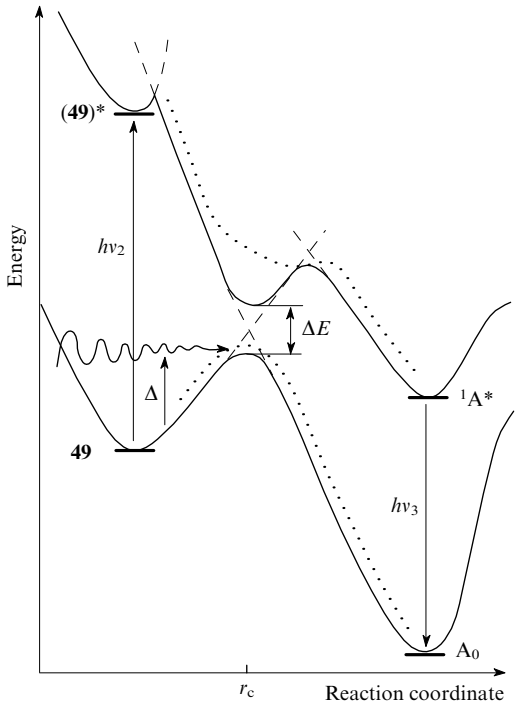
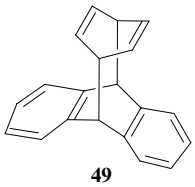
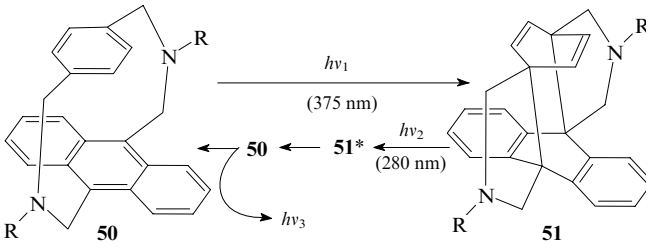


Figure 3. Cross-sections of the potential energy surface along the reaction coordinate at the thermolysis and the light-induced decomposition of heterodimer **49**.[142, 143]
A_0, $^1A^*$ are ground and excited singlet states of anthracene, r_c is the critical point.

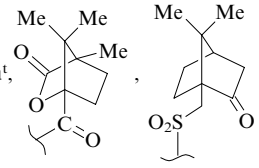
It was shown that the thermal decomposition of heterodimer **49** is a dark reaction, whereas its light-induced decomposition is accompanied by CL with the efficiency of chemical excitation of singlet anthracene of ~0.9! A scheme of energy levels in Fig. 3 shows that in the vicinity of the pericyclic minimum, the greatest part of energy of the absorbed photon is already consumed in reaction,[144] because the formation of a chemiluminescence photon consumes the chemical energy liberated in the decomposition of the heterodimer. Hence, in this case, the reason for the light emission is indeed chemiluminescence.



Synthesis of compounds containing photocyclisable aromatic fragments (*e.g.*, benzene and anthracene) linked with bridges,



R = C(O)Me, C(O)CF$_3$, C(O)Pr^i, C(O)Bu^t,



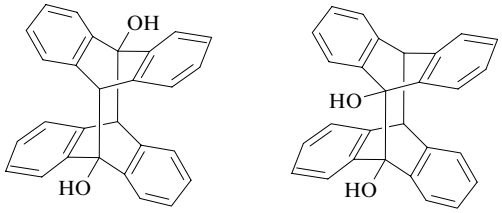
which makes them more flexible, was described.[145,146] This allowed the whole sequence of transformations, *viz*., cyclisation under illumination at 375 nm, recyclisation under illumination at 280 nm, chemical excitation and CL of the product, to be observed.

The introduction of substituents R into the bridge changes the distance between the planes of the benzene and anthracene fragments, which makes it possible to control the potential energy surface along the reaction route. The cross-section of the potential energy surface along the reaction route

$$\mathbf{51} + h\nu_2 \longrightarrow \mathbf{51}^* \longrightarrow \mathbf{50}^* \longrightarrow \mathbf{50} + h\nu_3$$

can also be represented by curves similar to those in Fig. 3 (the ground and excited states of molecule **50** correspond to species **49**, while those of molecule **51** correspond to anthracene).

The prohibition for the formation of excited products in the thermal reaction of photodimer decomposition can be substantially reduced (and even eliminated) if the reaction involves ionisation of molecules. It was shown [147,148] that the base-induced decomposition of anthrol photodimers **52** ('head-to-tail') and **53** ('head-to-head') is accompanied by CL with a spectrum similar to the fluorescence spectrum of the anthrol anion.



52 **53**

Earlier, chemiluminescence of photolysed solutions of anthrol was associated exclusively with CL of its peroxy derivatives.[149] The anthrol photolysis products were isolated by high-performance thin layer chromatography (HPTLC).[148] The R_f value of the substance that exhibits CL activity in the reaction with the base differs from the R_f of the peroxide, which was determined in its colour reaction with iodine. Reversed-phase HPTLC allowed better resolution of these bands. Chemiluminescence was observed for both the photodimer and peroxides, but the CL intensity of the photodimer proved to be more than 10 times higher.

Upon deprotonation, both hydroxyl groups in anthrol photodimers **52** and **53** (DA) decompose to two anthrol anions (E^-). Taking into account that the formation of two anthracene molecules with conjugated bond systems involves liberation of considerable energy, the DA decomposition product can exist in the electronically excited state

$$DA + OH^- \longrightarrow DA^- + H_2O,$$

$$DA^- + OH^- \longrightarrow (E^-)^* + E^- + H_2O,$$

$$(E^-)^* \longrightarrow E^- + h\nu.$$

In an ethanolic extract of dry *Hypericum perforatum* (St-John's wort), which can produce and accumulate various anthracene derivatives, a compound identical to the anthrol photodimer was detected using HPLC coupled with CL detection.

V. Analytical applications

Chemiluminescence analysis attracts steady interest among biologists and physicians and promises to become a routine test in many biological and medical laboratories.

The advances of nanotechnologies that employ 10–100-nm metal particles with 'extraordinary' properties as the transducers and amplifiers of fluorescence and CL open up new possibilities.[150,151] In light-created chemiluminescence systems, light plays the role of a cheap, available and convenient reactant.

Photosensitised CL of various chemiluminophores was employed for the assessment of the activity of superoxide dismutase and the antioxidant effect of different substances [33–39,41,42,59,63–70] and also in the chemiluminescence immunoassay.[32] Based on the detection of chemiluminescence that accompanies photooxidation, a new method of assessment of the state of rarities and historical objects and materials was proposed.[152,153] A method for studying photostability of polymers has been developed.[154–158]

Photochemical synthesis of dioxethanes and their use in the on-line kinetic analysis of alkenes were described.[111]

A highly selective ozone sensor was obtained by the photochemical modification of 4,5-dihydroxynaphthalene-2,7-disulfonic acid (chromotropic acid).[159]

Light-induced chemiluminescence systems were proposed for analysis of polyaromatic hydrocarbons,[74] pharmaceuticals [125,160,161] and pesticides.[123]

VI. Conclusion

Based on the material presented in this review, it follows that the problem of classification of light-created chemiluminescence systems is solved as soon as the mechanism of the light effect becomes clear.

Classification of 'parental' photochemical mechanisms already exists. Nowadays, in light-created chemiluminescence systems, the 'parental' mechanisms are represented by various kinds and types of photooxidation, structural photoisomerisation, phototransfer of protons (hydrogen atoms) and photodimerisation.

Any other classification unrelated to the mechanism of the chemical effect of light would be arbitrary, *e.g*., a classification based on the differences in the CL kinetics. The authors who proposed a new term 'photostorage CL' [114] distinguished this phenomenon from the others by the fact that the former does not exhibit any afterglow decay upon the effect of light but requires to be initiated by a base. We assume this difference insignificant. Indeed, if we change the experimental conditions, namely, add the base to solution beforehand and use pulse light, then the CL kinetics will take the form of afterglow decay.

One cannot but state the similarity in the response of different scientists to their first encounter with light-created chemiluminescence systems. First, this is bewilderment caused by the lack of understanding of the reasons for the scatter of experimental results on CL reactions, then, astonishment when one becomes aware that solutions prepared or stored for a long time in darkness do not provide a chemiluminescence reaction. Moreover, the efficiency of common laboratory illumination seems strange.

However, photochemical activity of ordinary illumination should not surprise. In the ordinary illumination, more than 10^{13} photons pass through an area of 1 cm^2 per second, which is 10^9 times greater than the detection limit of laboratory chemiluminometers; hence, the formed gap can be occupied by numerous chemical systems for which the multiplied efficiencies of absorption, photochemical transformation and chemiluminescence of the product are no less than 10^{-9}.

After the discovery of the key role of oxygen in luminescence and photochemical reactions, the scientists became very much aware of the presence of dissolved oxygen. Now that a sufficiently large number of chemiluminescence systems have been studied, it is time to become aware of the role of illumination conditions during the preparation of solutions and reaction mixtures.

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