

Invited Review

Efficiency of Electron Transfer Initiated Chemiluminescence[†]

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ABSTRACT

Although the mechanisms of many chemiluminescence (CL) reactions have been intensively studied, no general model has been suggested to rationalize the efficiency of these transformations. To contribute to this task, we report here quantum yields for some well-characterized CL reactions, concentrating on recent reports of efficient transformations. Initially, a short review on the most important general CL mechanisms is given, including unimolecular peroxide decomposition, electrogenerated CL, as well as the intermolecular and intramolecular catalyzed decomposition of peroxides. Thereafter, quantum yield values for several CL transformations are compiled, including the unimolecular decomposition of 1,2-dioxetanes and 1,2-dioxetanones, the catalyzed decomposition of appropriate peroxides and the induced decomposition of properly substituted 1,2-dioxetane derivatives. Finally, some representative examples of quantum yields for complex CL transformations, like luminol oxidation and the peroxyoxalate reaction, in different experimental conditions are given. This quantum yield compilation indicates that CL transformations involving electron transfer steps can occur with high efficiency in general only if the electron transfer is of intramolecular nature, with the intermolecular processes being commonly inefficient. A notable exception to this general rule is the peroxyoxalate reaction which, also constituting an example of an intermolecular electron transfer system, possesses very high quantum yields.

INTRODUCTION

Chemical transformations which liberate the reaction energy in the form of visible light are called chemiluminescence (CL) reactions, whereas the emission of light by living organisms is called bioluminescence (BL) (1). CL transformations are nowadays part of undergraduate textbooks (2,3) and can be utilized as stimulating experiments in undergraduate classes (4–6). Most of the efficient CL transformations are highly exothermic and occur in a complex sequence of reaction steps, as is the case of the luminol oxidation, first described by Albrecht almost a hundred years ago (7), the lucigenin CL (8), the oxidation of lophine (2,4,5-triphe-

nylimidazole) (9) and the peroxyoxalate reaction, first described by Chandross (10) and further developed by the Rauhut research group (11). However, the mechanism of these transformations, consisting of various sequential and parallel reaction steps, is not yet well known in most cases, specifically with respect to the chemiexcitation step, where the chemical reaction energy is transformed into electronic excitation (12). In most cases, even the structure of the essential intermediate formed in the reaction sequence which is responsible for electronic excitation, the so-called high-energy intermediate (HEI) is not exactly known, as is the case of all the transformations named above (12). However, mechanistic studies on CL transformations have been impacted strongly when it was possible to synthesize model compounds for these HEIs and to study their CL properties (13,14).

Important parameters to be determined in mechanistic studies on CL transformations are the CL quantum yields and/or the singlet and triplet excitation quantum yields. The influence of the reactant structures and reaction conditions on these quantum yields may give important information with respect to the reaction mechanism (12). In this review article, we give a short overview on the most important general chemiexcitation mechanisms, unlike other revisions that addressed only aspects of the induced decomposition of 1,2-dioxetanes (15,16), and show a compilation of chemiexcitation quantum yields of a series of important CL transformations, focusing mainly on examples with well-known reaction mechanisms and which involve electron transfer steps in the chemiexcitation sequence. In addition, CL quantum yields of some well-known complex reactions are given in several experimental conditions.

GENERAL MECHANISMS FOR EXCITED STATE GENERATION

Unimolecular peroxide decomposition

The unimolecular decomposition of 1,2-dioxetanes (**1**) and 1,2-dioxetanones (α -peroxylactones) (**2**) constitutes an example of a highly exothermic thermal reaction that leads to the formation of one of the product molecules in the electronically excited state (17). This process apparently occurs in a single elementary step, where cleavage of the weak peroxidic bond leads to the relief of ring strain by opening of the four-membered ring. These compounds can be synthesized and isolated, enabling mechanistic studies of their chemiluminescent transformations for the

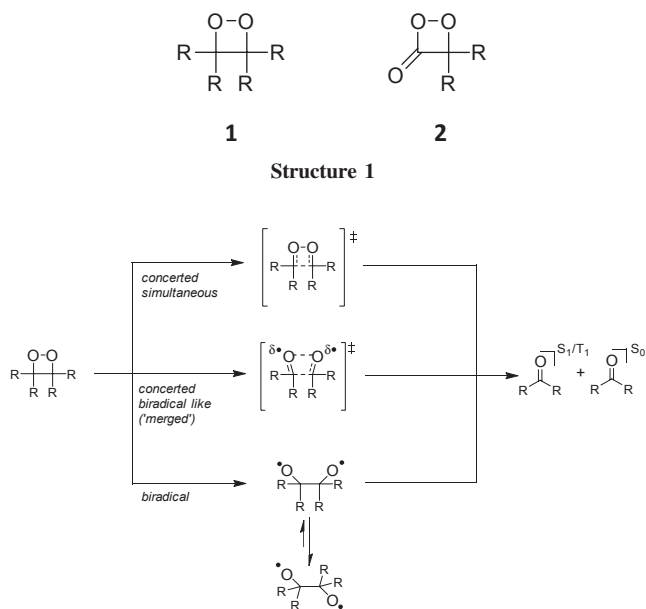
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elucidation of their chemiexcitation step. In the 1970s and 1980s, several 1,2-dioxetane derivatives and some 1,2-dioxetanones were synthesized and their chemiluminescent parameters upon unimolecular decomposition determined, indicating that these cyclic peroxides lead mainly to the formation of triplet excited states, with quantum yields of up to 30%, and very low production of singlet excited states, with quantum yields of <0.1% (18–27). Therefore, CL emission quantum yields (Φ_{CL}) in these transformations are low, as triplet excited states possess low emission quantum yields, due to preferential deactivation by nonradiative processes.

Two extreme mechanisms have been proposed for the unimolecular 1,2-dioxetane decomposition: the concerted mechanism (28,29), in which the cleavages of the O-O and C-C bonds occur simultaneously and the biradical mechanism (30,31), where the peroxide bond is initially cleaved and a 1,4-dioxy biradical formed, leading to the formation of a carbonyl compound in the singlet excited or the ground state. In addition, an intersystem crossing (ISC) may occur and a 1,4-dioxy biradical may be generated in its triplet excited state (32,33); consequently, a triplet excited carbonyl compound may be formed after rupture of the C-C bond (Scheme 1). Both mechanisms involve changes in spin multiplicity, but ISC in the biradical mechanism is believed to be reversible while it appears to be irreversible in the concerted mechanism (34). The biradical mechanism is appropriate to explain the activation parameters of 1,2-dioxetane decomposition (35); however, it is not able to rationalize the singlet and triplet quantum yields. Therefore, an intermediate mechanism has been proposed, in which the rupture of the O-O and C-C bond is concerted, but they do not occur simultaneously (Scheme 1) (36). This merged mechanism maintains the kinetic aspects of the biradical mechanism and is able to explain the formation of the electronically excited product on the same basis of the concerted mechanism, therefore being able to rationalize the activation parameters and excitation quantum yields of different 1,2-dioxetane derivatives.



Scheme 1. Proposed mechanisms for unimolecular decomposition of 1,2-dioxetanes: concerted simultaneous, concerted biradical like and biradical.

The relative stabilities and the excitation quantum yields obtained in the unimolecular decomposition of the series of methyl-substituted 1,2-dioxetanes, including the unsubstituted derivative (37), could be rationalized on the basis of a qualitative quantum mechanics model (36), indicating that a concerted, almost synchronized decomposition pathway should lead to high triplet and singlet quantum yields, whereas a biradical-like decomposition pathway would be expected to lead to low chemiexcitation quantum yields (Fig. 1) (36–39).

More recent experimental and theoretical studies showed that 1,2-dioxetanes substituted with bulky groups are more stable (35). The most stable 1,2-dioxetane synthesized is the bis-adamantyl-1,2-dioxetane (**1a**) and it was also shown that one adamantyl group is capable of stabilizing a series of 1,2-dioxetanes (*e.g.* **1b** and **1c**), which have a vast number of analytical applications (40–43). This stabilization is related to the structure of the four-membered ring, where, while the O-O bond is not broken, the bulky groups are kept away from each other. However, during the cleavage of the peroxidic bond, accompanied by rotation of the central C-C bond, these groups approach and compress each other (35).

It should still be mentioned that the unimolecular decomposition of 1,2-dioxetanones **2** also occurs with very low singlet quantum yields and triplet excited states are preferentially formed, although generally in lower yields than in 1,2-dioxetane decomposition (21,44).

In summary, the unimolecular decomposition of organic peroxides was shown to be a low efficient CL process, as the compounds are preferentially deactivated by nonradiative pathways or are quenched by molecular oxygen dissolved in the reaction medium. In addition, the singlet excited carbonyl compounds, aside from being formed in low yields, are known to possess considerably low fluorescence quantum yields ($\Phi_{FL} < 10^{-3}$) (1,18,19,24–26).

Electrogenerated CL

The process of electrogenerated CL or electrochemiluminescence (ECL) is, in principle, a very simple way to generate

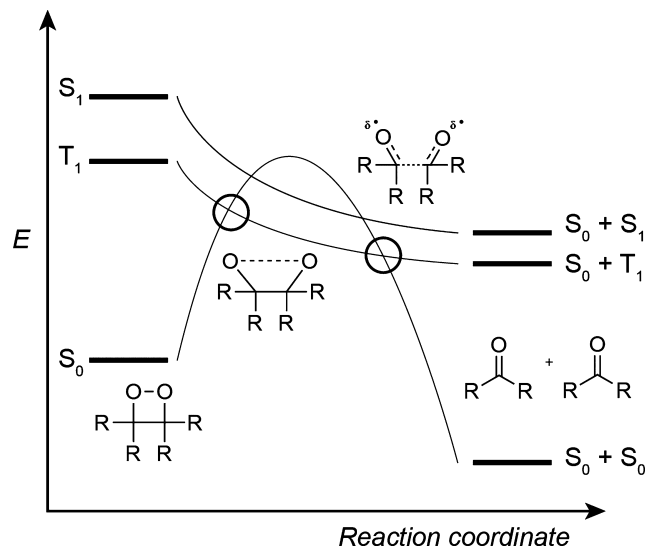
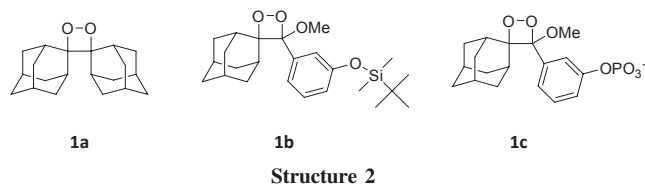
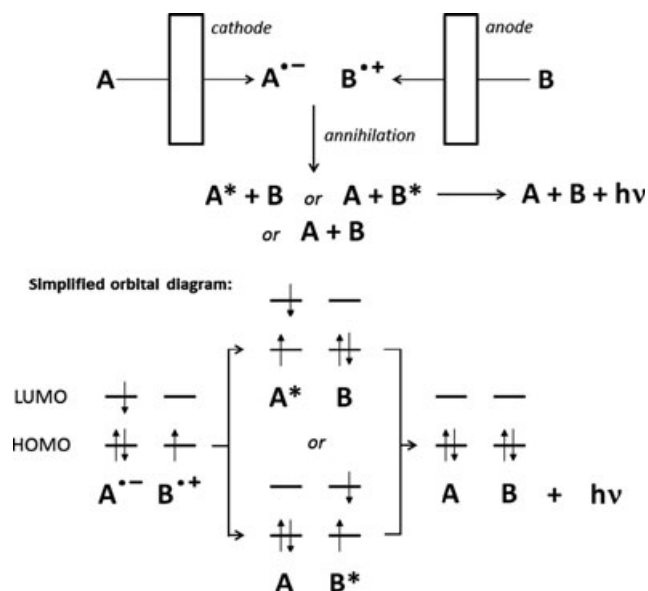


Figure 1. Potential energy curves for unimolecular 1,2-dioxetane decomposition in the ground state (S_0), triplet (T_1) and singlet (S_1) excited states.



electronically excited states in solution (45). This process was first described in the 1960s and nowadays two methods are well known and have widely accepted mechanisms proposed (46–49): ion annihilation ECL and coreactant ECL (45).

The coreactant ECL, a process in which a second substance is oxidized or reduced producing intermediates that eventually react with the species of interest, leading to excited state formation and subsequent emission of light, is widely used as an analytical tool (45). However, the ion annihilation ECL (Scheme 2) is described here in more detail, as this process can be regarded as the basis for the chemically initiated electron exchange luminescence (CIEEL) mechanism, thought to occur in the catalyzed decomposition of organic peroxides (50). The ECL process is initiated by the electrochemical generation of a radical cation at the anode and a radical anion at the cathode. These radical ions can diffuse toward each other in solution and annihilation will lead to regeneration of the initially involved species A and B (Scheme 2) (51). However, this electron transfer process can also lead to the formation of electronically excited states, as radical annihilation can liberate sufficient energy for chemiexcitation. When the electron is transferred from the former LUMO of the radical anion $A^{\bullet-}$ to the LUMO of $B^{\bullet+}$, this species is formed in its excited state (Scheme 2, below). However, when the electron is transferred from the former HOMO of $A^{\bullet-}$ to the HOMO of $B^{\bullet+}$, the former radical anion species A is formed in its excited state (Scheme 2, above) (51).



Scheme 2. General mechanism for excited state generation by ion annihilation electrochemiluminescence, where A and B can be the same or different species.

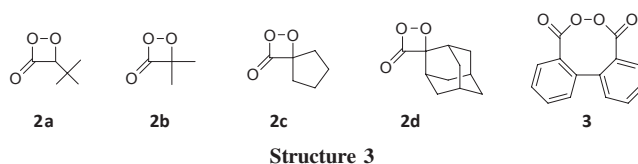
Catalyzed peroxide decomposition—Intermolecular reactions

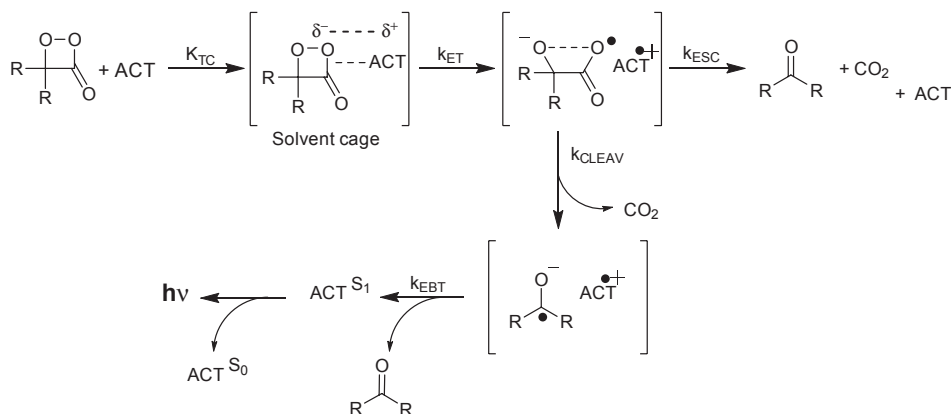
The low thermal stability of 1,2-dioxetanones (**2**) as well as the difficult synthesis of these cyclic peroxides (**52**) have restricted mechanistic studies on their chemiluminescent decomposition and the determination of the activation parameters and chemiexcitation quantum yields (12,53). In fact, until very recently, 3-*tert*-butyl-1,2-dioxetanone (**2a**) and 3,3-dimethyl-1,2-dioxetanone (**2b**) were the only derivatives synthesized, characterized and that had their CL properties extensively studied by the research groups of G.B. Schuster, W. Adam and N. J. Turro in the 1970s (12,14,44,50,54–57). Only more recently other derivatives (**2c** and **2d**) have been synthesized and their CL properties studied (see below) (52,53).

Similar to the case of 1,2-dioxetanes, the unimolecular decomposition of 1,2-dioxetanones proved to be an inefficient CL system, as triplet excited state products are formed predominantly, with very low singlet excited carbonyl production. Therefore, the unimolecular decomposition of these peroxides cannot be regarded as an adequate model system for the highly efficient bioluminescent systems (18). However, in the presence of polycondensed aromatic hydrocarbons with low oxidation potential (E_{ox}) and high fluorescence quantum yields (Φ_{FL}), the so-called activators (ACT), the decomposition rates, the emission intensities and the CL quantum yields were shown to be significantly enhanced (12,14,44,50,54–57).

On the basis of experimental results obtained in the catalyzed decomposition of isolable peroxides, such as diphenoyl peroxide (**3**) (22,26,50) and the 1,2-dioxetanone derivative **2b** (44,54–57), Schuster and coworkers formulated a chemiexcitation mechanism involving a rate-limiting electron transfer from the ACT to the organic peroxide, called the CIEEL mechanism (22,26). The occurrence of the rate-limiting initial electron transfer has been evidenced by the dependence of the observed rate constant on the ACT concentration and the fact that this rate constant also depends on the oxidation potential of the ACT.

The intermolecular CIEEL sequence is initiated by the formation of a charge transfer complex (K_{TC}) between, for example, the 1,2-dioxetanone and the ACT (Scheme 3). In this complex, O–O bond stretching results in an energy decrease of the antibonding σ^* orbital, facilitating electron donation from the ACT to the peroxide (k_{ET}) accompanied by the O–O bond cleavage, thereby making the electron transfer essentially irreversible (12,26). The 1,2-dioxetanone anion radical undergoes subsequent C–C bond cleavage (k_{CLEAV}) resulting in a neutral carbonyl compound and a new radical anion species still inside the solvent cavity (Scheme 3). This new pair of radical ions, a carbonyl radical anion and the ACT radical cation, still inside the solvent cage, undergoes an electron back-transfer (k_{EBT}), which may lead to the singlet excited state of the ACT (S_1). Fluorescence emission from the singlet excited ACT reestablishes this species in its ground state and constitutes the observed CL of the system (Scheme 3). For efficient excited state formation, the whole



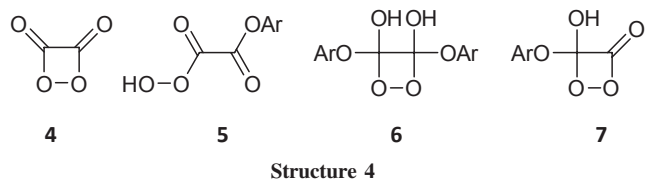


Scheme 3. Intermolecular chemically initiated electron exchange luminescence mechanism for the reaction of a 1,2-dioxetanone with an activator.

reaction sequence must occur inside the solvent cavity, because upon cage escape of the radical ion species (k_{ESC}); these would not encounter each other again to allow excited state formation by this process.

This chemiexcitation mechanism has been applied to a variety of other CL systems and experimental evidence on its validity has been accumulated by several research groups (12). However, it was also shown that the efficiency of excited state generation in the catalyzed decomposition of diphenoyl peroxide had been overestimated initially and proved to be several orders of magnitude lower than originally reported (50,58). This fact has been recently confirmed by our research group and it was shown that the quantum yields in the catalyzed decomposition of 1,2-dioxetanones are also considerably lower than initially reported (44,53–57).

However, it is well known that the base-catalyzed reaction of certain activated aromatic oxalic esters, like bis(2,4,6-trichlorophenyl) oxalate (TCPO), with hydrogen peroxide in the presence of an appropriate ACT leads to highly efficient light emission and quantum yields for this transformation were shown to be very high (11,59,60), with reported values of more than 60% (59). The kinetics of the peroxyoxalate reaction, first described by Chandross (10), has been studied by several research groups and different peroxide intermediates (4–7) have been postulated as high-energy compounds responsible for excited state formation (61–63). More recently, experimental evidence has been obtained in favor of 1,2-dioxetanedione (4) as the HEI in this reaction (64–66).



Experimental evidence showing the occurrence of an electron transfer from the ACT to the HEI in the peroxyoxalate reaction has been obtained using photophysical methods (59,67). However, only recently has it been possible to observe the reaction between an accumulated high energy intermediate and the ACT directly by kinetic measurements (68). These results indicate the occurrence

of the intermolecular CIEEL mechanism in the chemiexcitation step of the highly efficient peroxyoxalate reaction (69).

Induced 1,2-dioxetane decomposition—Intramolecular reactions

It has been shown above that the intermolecular CIEEL mechanism, although widely used to rationalize excited state formation in a variety of CL and BL systems, appears to be of low efficiency, at least in several of its model systems (53). There is, however, a variation of the CIEEL mechanism that can generate excited states efficiently (up to 100%) (70–72), called intramolecular CIEEL, due to the fact that the electron transfer to the peroxide bond occurs from a moiety within the same molecule. This kind of mechanism occurs with some 1,2-dioxetane derivatives, which contain an internal electron rich moiety. In general, this class of compounds contains the cyclic peroxide unit as an energy source, as well as a fluorophore, responsible for final light emission and an electron-rich moiety which can be generated, preferentially, by the action of a chemical agent, acting as a trigger. This class of compounds is represented by 1,2-dioxetane derivatives 8 and 9, which are structurally similar to the HEI formed from firefly luciferin, the model system to rationalize efficient BL (Fig. 2) (70–72).

Several 1,2-dioxetane derivatives, containing nitrogen or sulfur atoms directly linked to the peroxidic ring or in conjugation with it through acridinium or indolic moieties, synthesized in the 1970s, proved to be highly unstable and showed relatively high singlet excitation yields (Fig. 3) (73–84). Although these compounds could not be isolated and completely characterized in most cases, the occurrence of an intramolecular electron transfer from the electron-rich heteroatom to the peroxidic ring has been proposed to rationalize the low stability of these compounds (85). Shortly afterward, an intramolecular electron transfer from the phenolic unit to the peroxide bond in the firefly luciferin HEI 10 was postulated for excited state generation according to the intramolecular version of the CIEEL (86). An extremely important breakthrough with respect to application of 1,2-dioxetanes in analytical assays was initiated by the experimental observation of Schaap and coworkers that 1,2-dioxetane derivative 8 (70) (Fig. 2), a reasonable stable compound leading to preferential triplet state formation upon thermal decomposition, when deprotonated showed extremely fast decomposition and preferential singlet excited state formation in high yields (70).

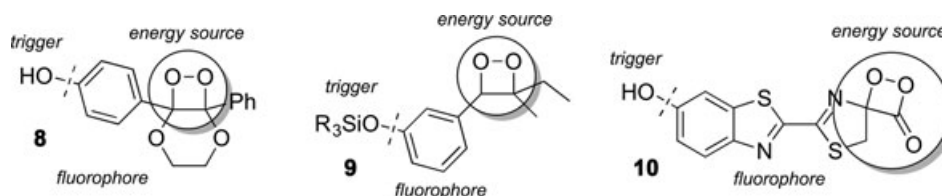


Figure 2. 1,2-Dioxetanes **8** and **9** which are model systems for intramolecular chemically initiated electron exchange luminescence (CIEEL) and the high-energy intermediate in firefly bioluminescence **10**, with the indication of the three elementary units necessary for efficient intramolecular CIEEL (70–72).

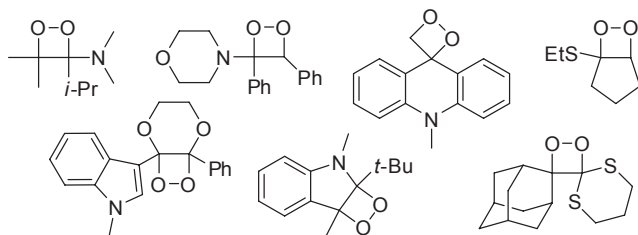


Figure 3. Some highly unstable 1,2-dioxetanes containing substituents with electron rich heteroatoms (73–84).

This initial experimental observation led to the synthesis of 1,2-dioxetane derivatives containing protected electron-rich moieties, which could be liberated by deprotection using appropriate triggering agents. The most utilized electron-rich group which could be liberated by deprotection is the phenolate unit, which might perform an intramolecular electron transfer to the cyclic peroxide bond (40,70,87,88). The formation of the phenolate can occur by simple deprotonation of a phenolic unit (70). Alternatively, it might be formed by fluoride-catalyzed deprotection of silyloxy-substituted aromatic compounds (88). In addition, deprotection can be performed by enzymatic catalysis, when utilizing acetate or phosphate-protected phenolic derivatives (40,87). The last type of deprotection has led to the development of a huge amount of detecting systems for immunoassays utilized in clinical analysis (41–43).

The decomposition of these 1,2-dioxetanes is initiated by the deprotection reaction with the appropriate triggering agent, leading to the formation of the phenolate ion. The electron-rich phenolate oxygen atom acts as an intramolecular electron donor to the peroxide bond leading to the concomitant cleavage of the labile O–O bond (ET, Scheme 4) (71,72), a process which has been recently confirmed experimentally (89,90). The biradical anion formed undergoes C–C bond cleavage, generating a neutral carbonyl compound and a new biradical anion fragment (Cleav., Scheme 4). This biradical anion can undergo a formal intramolecular electron back transfer leading to the formation of the phenolate in its electronically excited singlet state (EBT, Scheme 4), which can return to the ground state with fluorescence emission, completing the CL process (Scheme 4) (71,72,91).

Quantum yields in CL transformations

In this part of the article, we will give quantum yields determined in the literature for several of the model CL transformations whose mechanisms have been well investigated. Furthermore, the quantum yields for some of the complex CL transformations will be given in the last part.

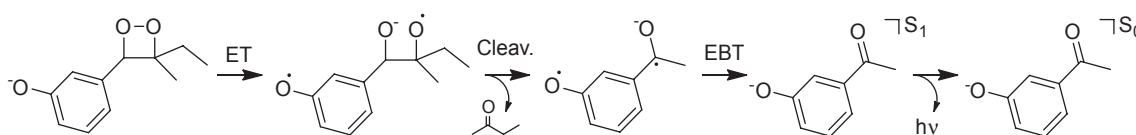
The CL quantum yield (Φ_{CL}) can be most simply defined as the relation between the number of photons emitted by a certain chemical reaction (in Einstein, E) per number of moles of limiting reactant (Eq. 1). This quantum yield is composed by the quantum yield of excited state formation by the chemical reaction—singlet quantum yield (Φ_{S}) or triplet quantum yield (Φ_{T}), depending on the multiplicity of the excited state formed—and the emission quantum yield of the electronically excited species—fluorescence quantum yield (Φ_{F}) for singlet species or phosphorescence quantum yield (Φ_{Ph}) for triplet species (Eqs. 2 and 3) (12,92). In aerated solution, usually only fluorescence emission will be observed, therefore efficient CL can only be expected from reactions forming singlet excited states ($\Phi_{\text{CL}}^{\text{S}}$) and those forming triplet excited states ($\Phi_{\text{CL}}^{\text{T}}$) will normally be non-emissive (12,92).

$$\Phi_{\text{CL}} = \frac{\text{number of photons emitted}}{\text{mols of Limiting reagent}} \quad (1)$$

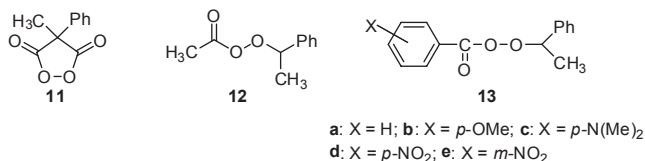
$$\Phi_{\text{CL}}^{\text{S}} = \Phi_{\text{S}} \times \Phi_{\text{F}} \quad (2)$$

$$\Phi_{\text{CL}}^{\text{T}} = \Phi_{\text{T}} \times \Phi_{\text{Ph}} \quad (3)$$

The CL quantum yields can be determined experimentally by integration of the kinetic emission intensity curve and the numerical value of this integral (generally expressed in arbitrary units) can be transformed in number of photons (in Einstein) by the use of calibration factors determined with appropriate reference CL systems as the luminol reaction (12). The main calibration methods used in the determination of CL quantum yields are described in detail in the Supporting Information (93–96). The quantum yields are obtained subsequently by correlation of the total amount of photon emitted by the chemical reaction with



Scheme 4. Simplified intramolecular chemically initiated electron exchange luminescence mechanism proposed for the induced decomposition of 1,2-dioxetane **9** after generation of the phenolate by deprotection (71,72).



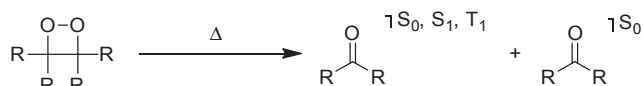
Structure 5

the number of moles of limiting reactant transformed (Eq. 1). The singlet excitation yields can be obtained from the CL quantum yields by using the fluorescence emission quantum yields of the emitting species (Eq. 2).

Quantum yields in unimolecular peroxide decomposition: 1,2-dioxetanes and 1,2-dioxetanones

The decomposition of 1,2-dioxetanes (**1**) and 1,2-dioxetanones (**2**) has been studied mainly in the 1970s and early 1980s and several hundreds of 1,2-dioxetane derivatives have been studied. However, due to the much more difficult synthesis of these peroxides, no more than ten 1,2-dioxetanones have been synthesized and their thermal stability data and quantum yields determined (12,92). The thermal decomposition of these cyclic four-membered ring peroxides occurs by unimolecular kinetics and can lead to the formation of one of the two carbonyl products in its electronically excited singlet or triplet state (Scheme 5).

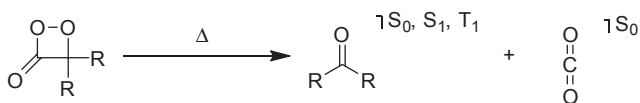
The 1,2-dioxetane derivative most intensively studied is the



Scheme 5. Thermal decomposition of a 1,2-dioxetane (**1**) into two carbonyl products.

tetramethyl-1,2-dioxetane and the quantum yields determined are in the range of $\Phi_S \sim 2 \times 10^{-3}$ E mol⁻¹ and $\Phi_T \sim 0.3$ E mol⁻¹, leading to Φ_T/Φ_S ratios higher than one hundred and most other 1,2-dioxetane derivatives behave in a similar way (92). It has been shown that substitution of the methyl group for a hydrogen atom leads to a decrease in singlet and triplet quantum yields, in parallel to a decrease in stability (27,37). This trend holds for most of the derivatives studied: the more stable the cyclic peroxide, the higher are the excitation quantum yields.

The unimolecular decomposition of 1,2-dioxetanones occurs in a similar manner, leading to the formation of carbon dioxide and a carbonyl compound which may be formed in the singlet or triplet excited state (Scheme 6). There are only a few studies on the unimolecular decomposition of these peroxides and the general trend here is that the triplet quantum yields for 1,2-dioxetanones are lower than for 1,2-dioxetanes, even though 1,2-dioxetanones liberate more energy upon thermal decomposition than 1,2-dioxetanes (12,21,44,92).



Scheme 6. Thermal decomposition of a 1,2-dioxetanone (**2**) into a carbonyl compound and carbon dioxide.

The quantum yields obtained in the thermal decomposition of 1,2-dioxetanes and 1,2-dioxetanones have been compiled in several review articles (12,92,97) and there are only a few studies reported in the last 10–15 years. In a study from our research group on the induced decomposition of phenoxy-substituted 1,2-dioxetanes, the quantum yields in the thermal decomposition of the silyl-protected derivatives have also been reported, which show to be within the range expected for tri-substituted derivatives (72).

Quantum yields in intermolecular CIEEL transformations

The intermolecular CIEEL mechanism has been mainly studied by the decomposition of diphenoyl peroxide and 1,2-dioxetanones catalyzed by appropriate ACT. However, other linear and cyclic peroxides (**11–13**) also have been utilized. The quantum yields for the decomposition of diphenoyl peroxide (**3**) and 3,3-dimethyl-1,2-dioxetanone (**2b**) have initially been reported as 0.10 E mol⁻¹ (44,50,54,55). However, the value for diphenoyl peroxide has been shown to be overestimated in various orders of magnitude thereafter (58). More recently, it has been shown also that the decomposition of the 1,2-dioxetanone derivative **2b** occurs with low quantum yields (Table 1) (53). Adam *et al.* (56) determined the CL quantum yield for the decomposition of **2a** ($\Phi_{CL} = 0.072$ E mol⁻¹) in the presence of rubrene (RUB) and obtained a value similar to that for **2b** determined initially by the Schuster group (Table 1). The recent study on the quantum efficiency in the catalyzed decomposition of the new 1,2-dioxetanone derivatives **2c** and **2d** proved that the CIEEL decomposition of these compounds occurs with very low quantum yields, thereby questioning the efficiency of intermolecular CIEEL transformations and casting doubts on its validity (53).

The singlet quantum yields in the catalyzed decomposition of malonyl peroxide (**11**) were estimated to be lower than 0.1% (Table 1) (98). The decomposition of peroxyesters **12** and **13** proved to occur, in general, with low singlet quantum yields. In some cases it was possible to obtain triplet quantum yields using 9,10-dibromoanthracene-sensitized CL (Table 1) (99), but these data have never been confirmed independently.

The peroxyoxalate reaction, on the other hand, occurs with extremely high quantum efficiency, as indicated by quantum yield determinations by various research groups, utilizing different calibration methodologies (Table 1) (11,59,60). The highest value reported up to now of $\Phi_S = 0.68$ E mol⁻¹ was obtained using RUB as a catalyst and indicates that two-thirds of limiting reactant molecules are generating an electronically excited state, an astonishingly high value taking into account that this system consists of a complex reaction sequence with innumerable possible side reactions. More quantum yield values of the peroxyoxalate system in a variety of experimental conditions will be given below.

In a general approach, the data above indicate that the decomposition of organic peroxides through the intermolecular CIEEL mechanism is not an efficient system for the generation of electronically excited species as the singlet quantum yields are generally very low. The notable exception is constituted by the peroxyoxalate reaction, with 1,2-dioxetanedione as the most probable HEI, which presented extremely high singlet quantum yields (Table 1).

Table 1. Excited state quantum yields generated through intermolecular chemically initiated electron exchange luminescence mechanism for several chemiluminescent systems.

System	$\Phi_S \times 100$ (E mol ⁻¹)	Cal.*	Refs
Diphenoyl peroxide (3)	10 ± 5	I	(50)
	(2 ± 1) 10 ⁻³	II	(58)
	(3.3 ± 0.2) 10 ^{-3†}	III	(53)
	(8.1 ± 0.5) 10 ^{-2‡}	III	(53)
3,3-Dimethyl-1,2-dioxetanone (2b)	10 ± 5	I	(54)
3-Tert-butyl-1,2-dioxetanone (2a)	0.10 ± 0.02 [§]	III	(53)
3-Tert-butyl-1,2-dioxetanone (2d)	7.2 [¶]	—	(56)
Spiro-adamantyl-1,2-dioxetanone (2d)	0.15 ± 0.09**	III	(53)
Spiro-cyclopentyl-1,2-dioxetanone (2c)	(3.9 ± 0.6) 10 ^{-2††}	III	(53)
	(1.3 ± 0.5) 10 ^{-2‡‡}	III	(53)
4-Methyl-4-phenyl-malonyl peroxide (11)	< 0.1 ^{§§}	—	(98)
1-Phenylethyl-peroxybenzoate (13c)	0.24 ^{¶¶}	I	(99)
1,2-Dioxetanedione (4)	23***	—	(11)
	15.8 ^{†††}	IV	(60)
	68 ± 5 ^{‡‡‡}	III	(59)

Triplet quantum yields (Φ_T) were calculated for **2a**, **12**, **13a** and **13c** and they correspond to 1.5×10^{-1} , 2×10^{-4} , 3.8×10^{-2} and 2×10^{-5} E mol⁻¹, respectively. *Calibration methods I: Through triplet yield of a solution of tetramethyl-1,2-dioxetane with 9,10-dibromoanthracene, II: According to Hastings-Weber procedure (93), III: modified method for the luminol standard (59), IV: absolute calibration (60); [†][**3**] = 1.0 mmol L⁻¹, [PER] = 0.5–5.0 mmol L⁻¹ in CH₂Cl₂ at 32.5°C; [‡][**3**] = 1.0 mmol L⁻¹, [RUB] = 0.1–1.0 mmol L⁻¹ in toluene at 25°C; [§][**2b**] = 0.11 mmol L⁻¹, [RUB] = 0.1–2.5 mmol L⁻¹ in CH₂Cl₂ at 25°C; [¶][**2a**] = 0.1 mmol L⁻¹, [RUB] = 1.3 mmol L⁻¹, in benzene; ** [**2d**] = 0.25 mmol L⁻¹, [RUB] = 1.0 mmol L⁻¹, in toluene at 35°C; ^{††}[**2c**] = 3.0 μmol L⁻¹, [RUB] = 1.0 mmol L⁻¹, in toluene at 25°C; ^{‡‡}[**2c**] = 3.0 μmol L⁻¹, [RUB] = 1.0 mmol L⁻¹, in ethyl acetate at 25°C; ^{§§}[**11**] = 2.1 mmol L⁻¹, [PER] = 1.0–3.0 mmol L⁻¹, in CH₃CN at 70°C, PER = perylene; ^{¶¶}[**13c**] = 0.1–0.3 mmol L⁻¹, [DBA] = 0.1 mmol L⁻¹, in benzene at 100°C; ***[DNPO] = 1.0 mmol L⁻¹, [H₂O₂] = 25 mmol L⁻¹, [RUB] = 0.5 mmol L⁻¹, in dimethyl phthalate at 25°C, DNPO: bis(2,4-dinitrophenyl) oxalate; ^{†††}[PCPO] = 3.0 mmol L⁻¹, [H₂O₂] = 0.4 mmol L⁻¹, [sodium salicylate] = 0.117 mmol L⁻¹, [DPA] = 5.0 mmol L⁻¹, in ethyl acetate at 25°C performed inside an actinometer cell containing a 0.15 mol L⁻¹ solution of potassium ferrioxalate under nitrogen atmosphere. PCPO: bis-(pentachlorophenyl) oxalate, DPA: 9,10-diphenylanthracene; ^{‡‡‡}[TCPO] = 0.1 mmol L⁻¹, [IMI-H] = 1.0 mmol L⁻¹, [H₂O₂] = 10 mmol L⁻¹, [RUB] = 0.1–2.0 mmol L⁻¹ in ethyl acetate at 25°C. IMI-H: imidazole.

Quantum yields in intramolecular CIEEL

Contrary to the behavior of the cyclic peroxides described before, simple alkyl and aryl-substituted 1,2-dioxetanes do not show catalyzed decomposition in the presence of an activator. However, during the 1970s and 1980s, a few 1,2-dioxetane derivatives containing electron-rich substituents were synthesized and studied. (80–83,100,101) These compounds proved to possess very low stability and much higher singlet quantum yields (Φ_S) and CL quantum yields (Φ_{CL}) than “simple” 1,2-dioxetanes (Table 2). The decomposition of these derivatives is believed to be initiated by an intramolecular electron transfer from the electron-rich moiety, in the examples shown mainly from the nitrogen lone pair, to the peroxidic ring, in an intramolecular version of the CIEEL mechanism. These compounds show Φ_S up to 0.5 E mol⁻¹ (Table 2, entry 3) and are very unstable, with half-lives reaching only a few seconds at 0°C (Table 2, entries 1 and 6). More recent examples selected include a highly efficient

and very unstable derivative with $\Phi_{CL} = 0.24$ E mol⁻¹ and another one with low efficiency (Table 2, entries 7 and 8) (102,103).

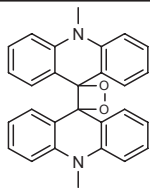
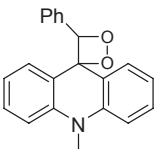
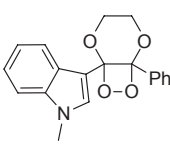
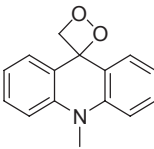
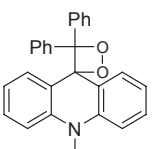
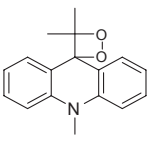
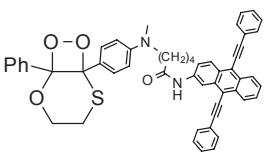
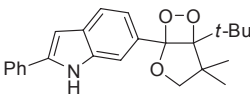
The studies on the intramolecular electron transfer initiated decomposition of appropriate 1,2-dioxetane derivatives advanced significantly with the discovery by the Schaap research group that the deprotonation of a phenoxy-substituted 1,2-dioxetane derivative leads to fast peroxide decomposition and efficient singlet excited state formation (70). The first derivative studied proved to be extremely unstable after deprotonation, with a half-life time of 50 ms at 25°C and a singlet quantum yield of 1.0 E mol⁻¹ (Table 3, entry 1). Thereafter, several 1,2-dioxetane derivatives with substituents containing aromatic hydroxyl groups have been synthesized and their CL properties after deprotonation studied (Table 3) (104–110). The selection of some 1,2-dioxetane derivatives studied (shown in Table 3) indicates that many of these derivatives possess high singlet quantum yields and very low stability. However, other derivatives proved to be more stable and some of the compounds possess low quantum yields (Table 3, entries 2, 3 and 7). More examples for hydroxyl-substituted 1,2-dioxetane derivatives which show induced decomposition by deprotonation are shown in Table S1.

The most important recent advance in mechanistic CL research and specifically for analytical application of induced 1,2-dioxetane decomposition has been achieved with the design of 1,2-dioxetane derivatives containing appropriate protective groups which can be removed by adequate chemical or enzymatic trigger reagents, generating the electron-rich moiety which initiates peroxide decomposition by intramolecular electron transfer (40,87,88).

Among these protective groups, the most adequate to be used for chemical studies of the induced 1,2-dioxetane decomposition is the trialkylsilyl group and many 1,2-dioxetane derivatives containing trialkylsilyl-protected aromatic hydroxyl groups have been synthesized and had their quantum yields upon induced decomposition determined (Table 4) (71,72,88,95,111–118). Many of the illustrative examples shown possess extremely high singlet and CL quantum yields and very low stability after removal of the protective group (Table 4). This is also true for the *spiro*-adamantyl-substituted derivatives (Table 4, entries 1–3), which possess, however, very high thermal stability (12,88,95,111). It can also be observed that the induced decomposition occurs also when the phenolic unit is not in conjugation with the peroxidic ring, with similar lifetimes, but with a much lower efficiency (Table 3, entry 6) (71,72). When the phenolic moiety is linked to the peroxidic ring by a C-C double or triple bond, CL quantum yields upon induced decomposition appear to be low in both cases. Interestingly, the derivative with the triple bond shows very fast decomposition kinetics, possessing, however, extremely low quantum yields, whereas the double bond derivative shows very slow decomposition and considerably higher quantum yields (Table 4, entries 8 and 9) (113).

Interestingly, the presence of two *iso*-propyl group on the peroxidic ring has shown to lead to a considerable increase in the thermal stability of these derivatives. Therefore this kind of compounds are interesting to substitute the *spiro*-adamantyl derivatives in analytical applications, as their induced decomposition also occurs with reasonably high emission quantum yields (Table 4, entries 9 and 10) (114,115). Bicyclic 1,2-dioxetane derivatives (Table 4, entries 12–15) (116–118) also proved to be

Table 2. Quantum yields ($E \text{ mol}^{-1}$) for the decomposition of some 1,2-dioxetanes containing electron-rich substituents.

Entry	Structure	Φ_{CL}	Φ_{S}	$t_{1/2}$ (s, 25°C)	Cal.*	Refs
1		1.6×10^{-2}	3.6×10^{-2}	12.4 [†]	V	(81)
2		—	2.5×10^{-1}	533	V	(82)
3		3.6×10^{-2}	5.0×10^{-1}	—	II	(84)
4		1.5×10^{-2}	3.4×10^{-2}	60 [‡]	V	(83)
5		1.4×10^{-1}	4.2×10^{-1}	≈1400	V	(100)
6		1.4×10^{-6}	—	60 [†]	II	(101)
7		2.4×10^{-1}	—	1.8	V	(102)
8		3.4×10^{-5}	8.7×10^{-5}	0.09	—	(103)

*Calibration methods: II: according to Hastings–Weber procedure (93) V: relative to the luminol standard (94); [†]half-lives at 0°C; [‡]half-life at –60°C.

of interest for potential analytical application, due to their high thermal stability and the high quantum yield obtained upon induced decomposition in some cases (Table 4, entry 12) (116). More examples for quantum yields obtained in the decomposition of silyl-protected 1,2-dioxetane derivatives are given in Table S2.

Finally, we report in this part quantum yields obtained in the triggered decomposition of 1,2-dioxetanes containing diverse protective groups, which are transformed into good elec-

tron donors after deprotection, or reactive groups, which are converted into electron donor groups by specific reagents (40,119–122). The most important 1,2-dioxetanes for bioanalytical applications are phosphate-protected derivatives which can be deprotected by the enzymatic action of phosphatases (Table 5, entries 1 and 2) (41–43). The quantum yields for the induced decomposition of these 1,2-dioxetanes proved to be very low in aqueous medium (Table 5). Even so, they can be utilized as highly sensible detection systems for alkaline phosphatase in

Table 3. Quantum yields ($E\ mol^{-1}$) for the decomposition initiated by deprotonation of some representative 1,2-dioxetane derivatives containing aromatic hydroxyl groups.

Entry	Structure	Φ_{CL}	Φ_S	$t_{1/2}$ (s, 25°C)	Cal.*	Refs
1		—	1.0	0.05	II	(70)
2		7.9×10^{-3}	—	12.0	VI	(104)
3		8.5×10^{-3}	1.4×10^{-2}	1.0	VI	(105)
4		1.5×10^{-1}	2.4×10^{-1}	≈ 5800	VI	(106)
5		1.2×10^{-2}	3.3×10^{-2}	26	VI	(107)
6		1.9×10^{-1}	—	7.8	VI	(108)
7		4.0×10^{-5}	—	45	VI	(109)
8		1.1×10^{-1}	4.9×10^{-1}	120	VI	(110)

*Calibration methods – II: according to Hastings–Weber procedure (93), VI: relative to 3-adamantylidene-4-(3-*tert*-butyl-dimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane (95,96).

innumerable immunoassays (41–43). Although there are much more examples of different protection and reactive groups used to induce 1,2-dioxetane decomposition, we report here only examples with exact quantum yields determined (Table 5). The quantum yields obtained in all these examples are considerably low, but they are interesting as they show that the induced 1,2-dioxetane decomposition can be achieved using diverse trigger functions.

CL quantum yields of complex reactions

In this part quantum yields are reported for some complex, highly efficient CL transformations, which had their mechanisms

studied, although not completely elucidated. The main reactions referred to are the luminol and the peroxyoxalate systems, which still are intensively studied and have a considerable volume of quantum yield data in a wide variety of experimental conditions (12). Only some data for quantum yields will be reported; no complete survey on this subject will be given.

The CL emission observed during the oxidation of 5-amino-2,3-dihydro-1,4-phthalazinedione was first described by Albrecht in 1928, and is considered one of the first CL transformations discovered (7). This reaction has found innumerable analytical and bioanalytical applications, being the first CL transformation utilized for the development of commercial analytical assay kits (123–128). The mechanism of the chemiluminescent oxidation of

Table 4. Quantum yields ($E\ mol^{-1}$) for the decomposition induced by fluoride deprotection of some representative examples of 1,2-dioxetane derivatives containing silyl-protected aromatic hydroxyl groups.

Entry	Structure	Φ_{CL}	Φ_S	$t_{1/2}$ (s, 25°C)	Cal.*	Refs
1		2.5×10^{-1}	5.7×10^{-1}	5.0	V	(89)
2		5.2×10^{-2}	2.4×10^{-1}	—	II	(111)
3		2.9×10^{-1}	6.6×10^{-1}	—	II	(95)
4		3.0×10^{-1}	6.8×10^{-1}	0.9	II	(95)
5		1.8×10^{-1}	—	48	VI	(112)
6		3.7×10^{-2}	1.0	11.0	—	(71,72)
7		7.4×10^{-5}	1.0×10^{-2}	16.0	—	(71,72)
8		2.6×10^{-4}	—	≈ 3000	—	(113)
9		3.0×10^{-7}	—	0.2	—	(113)
10		2.1×10^{-1}	—	6.3	VI	(114)
11		5.6×10^{-2}	—	≈ 250	VI	(115)
12		2.0×10^{-1}	—	4.6	VI	(116)

Table 4. (continued)

Entry	Structure	Φ_{CL}	Φ_{S}	$t_{1/2}$ (s, 25°C)	Cal.*	Refs
13		1.5×10^{-2}	2.1×10^{-1}	≈ 2500	VI	(117)
14		5.5×10^{-4}	—	3.8	VI	(118)
15		8.3×10^{-6}	—	0.03	VI	(118)

TBS = *tert*-butyldimethylsilyl. *Calibration methods: II: according to Hastings–Weber procedure (93), V: relative to the luminol standard (94), VI: relative to 3-aminotyridene-4-(3-*tert*-butyl-dimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane (95,96).

luminol is not yet fully understood. However, it is known that hydrogen peroxide is a necessary reagent for efficient CL emission; the reaction occurs with several different oxidizing species and is catalyzed by a vast range of transition metal ions (7). In addition, singlet excited 3-aminophthalate dianion has been identified as the emitting species and in aqueous medium the reaction occurs with reasonable velocity and emission intensity only in basic conditions. A general mechanism for this reaction in aqueous solution has been proposed by Merenyi *et al.* (129), consisting of three basic reaction steps: (1) oxidation of luminol monoanion and concomitant deprotonation to the corresponding anion radical; (2) further oxidation of the luminol radical to the diazaquinone derivative **14** followed by its reaction with the hydroperoxide anion or direct reaction of this radical anion with superoxide radical; both paths leading to the formation of a peroxyketal derivative **15**; (3) decomposition of the peroxide intermediate **15** to 3-aminophthalate and molecular nitrogen, accompanied by light emission (Scheme 7) (129). In addition, more detailed mechanistic schemes have been proposed to rationalize experimental observations in specific reaction conditions (130–132). However, peroxyketal derivative **15** is proposed as a key intermediate for the chemiluminescent pathway in all cases (133).

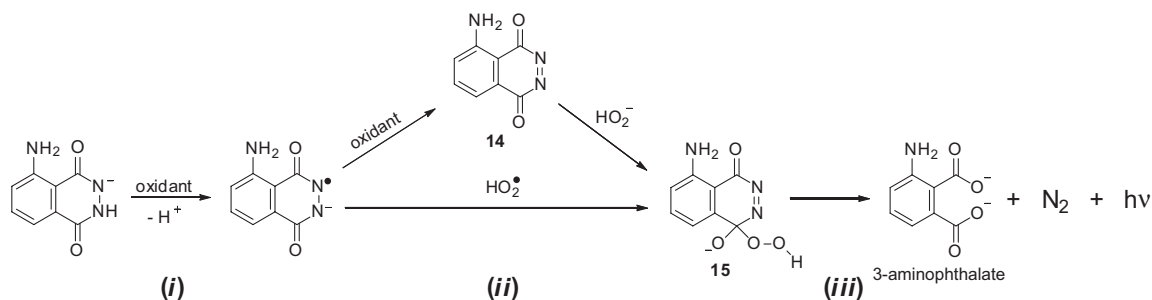
Contrary to the situation in the aqueous medium, luminol CL in aprotic solvents does not depend on hydrogen peroxide to be efficient and it is believed that molecular oxygen participates in the reaction sequence (12). The reaction sequence is believed to be initiated by the addition of molecular oxygen to the luminol

dianion, leading to a peroxidic intermediate **16**, whose structure is still unknown, which is transformed in molecular nitrogen and 3-aminophthalate in its singlet excited state, followed by light emission (Scheme 8) (134,135).

The CL oxidation of luminol in aqueous medium has been studied using a variety of different oxidants and catalysts. We report here quantum yields available in the literature in some typical reaction conditions (Table 6) (94,136–144).

Several studies have shown that the pH optimum for this reaction is between pH 11 and 13, and most studies are performed in these conditions (12). The quantum yields obtained are not affected by reagent concentrations, temperature, solvent polarity and viscosity. For example, the quantum yields for luminol oxidation were determined as 0.0124, 0.012 and 0.012 E mol^{−1} in pure water, water/propylene glycol (1:1) and water/propylene glycol (1:9), respectively. These results indicate that solvent viscosity does not affect the quantum yield of the luminol CL (143). Quantum yields are more significantly changed with different oxidants; however, they proved to be between 0.01 and 0.02 E mol^{−1} in most experimental conditions (Table 6). Moreover, in a comparative study, quantum yields of 0.0001, 0.004 and 0.007 E mol^{−1} were reported for the luminol reaction in otherwise identical conditions on using K₃Fe(CN)₆, NaOCl and K₂S₂O₈, respectively, as oxidants (143,144).

Quantum yields have also been reported for the oxidation of luminol (**17**) and isoluminol (**18**) derivatives, using hemin and hydrogen peroxide in aqueous bicarbonate solutions (Table 7)

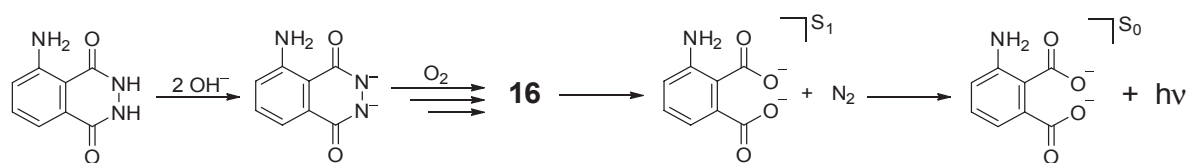


Scheme 7. General mechanistic scheme for the chemiluminescent oxidation of luminol in aqueous solution (133).

Table 5. Quantum yields ($E \text{ mol}^{-1}$) for the decomposition of some representative examples of 1,2-dioxetane derivatives containing different trigger functions, induced by functional group modification.

Entry	Structure	Φ_{CL}	Φ_{S}	$t_{1/2}$ (s, 25°C)	Cal.*	Refs
1		7.5×10^{-6}	—	60 [†]	II	(119)
2		5.7×10^{-6}	—	— [‡]	II	(119)
3		1.4×10^{-6}	3.0×10^{-6}	— [‡]	V	(40)
4		4.2×10^{-6}	—	219	II	(120)
5		5.7×10^{-6}	—	0.2	—	(121)
6		5.7×10^{-3}	3.2×10^{-1}	≈2300	VI	(122)

*Calibration methods – II: according to Hastings–Weber procedure (93), V: relative to the luminol standard (94), VI: relative to 3-adamantylidene-4-(3-*tert*-butyl-dimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane(95,96); [†]half-life at 37°C in pH 12.7; [‡]half-life for induced decomposition not reported.



Scheme 8. General mechanism for the chemiluminescent oxidation of luminol in basic aprotic solvents (134,135).

(145). These data indicate that alkyl substitution on the aromatic ring of luminol does not change significantly the quantum yields and the considerably lower quantum yields for isoluminol and derivatives (Table 7) (145).

Quantum yield values have also been reported for the reaction of lucigenin (10,10'-dimethyl-9,9'-biacridinium salt) with hydrogen peroxide in alkaline media and were shown to be similar to those obtained with luminol (12). The quantum yields were shown to be independent of the hydrogen peroxide concentration (excess concentration of 6–100 mmol L⁻¹) and varied only

slightly with the pH for values above pH = 11 ($\Phi_{\text{CL}} = 8.7 \times 10^{-3} E \text{ mol}^{-1}$ at pH = 11.3 and $\Phi_{\text{CL}} = 1.0 \times 10^{-2} E \text{ mol}^{-1}$ at pH = 12.4) (146).

The peroxyoxalate reaction is one of the brightest CL reactions known and is widely used in practical (“light-sticks”) and analytical applications (147). The reaction was shown to occur with high quantum yields in favorable conditions and is the only well characterized CL transformation (11,59,60), which was shown to occur by an intermolecular CIEEL mechanism, with proven high quantum yields (53).

Table 6. Chemiluminescence quantum yields (Φ_{CL}) for luminol oxidation in aqueous medium with different oxidants and catalysts.

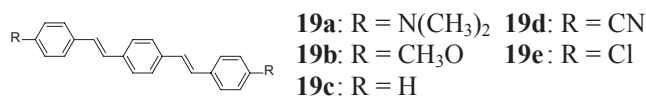
Oxidant/catalyst	pH	Φ_{CL} ($E \text{ mol}^{-1}$)	Refs
OH^{\bullet}	10	2.4×10^{-2}	(136)
$H_2O_2/NaOCl$	11	2×10^{-2}	(137)
$H_2O_2/hemin$	14.5	1.5×10^{-2}	(138)
$H_2O_2/hemin$	11.5	1.28×10^{-2}	(139)
$H_2O_2/hemin$	11.6	1.25×10^{-2}	(94)
$H_2O_2/hemin$	11.6	1.24×10^{-2}	(140)
H_2O_2/HRP	11.5	1.23×10^{-2}	(141)
$H_2O_2/met\text{-hemoglobin}$	11	1.02×10^{-2}	(142)
H_2O_2	11.6	1.14×10^{-2}	(94)
$K_2S_2O_8$	11.6	7×10^{-3}	(143)
$K_3Fe(CN)_6/H_2O_2$	13	2.5×10^{-3}	(144)

This reaction is still investigated for mechanistic elucidations and various analytical applications and we give here only some illustrative recent examples of quantum yields for this transformation in different experimental conditions. The high quantum yield values initially reported by the Rauhut research group for the peroxyoxalate reaction (11) have been confirmed independently by an absolute determination of the quantum yields in this reaction with bis(pentachlorophenyl) oxalate, using 9,10-diphenylanthracene (DPA) as activator (Table 8) (60). Quantum yields of the peroxyoxalate reaction with TCPO in ethyl acetate as solvent and imidazole as nucleophilic base were reported with different ACT and values for the singlet quantum yields as high as $\Phi_S = 0.68 E \text{ mol}^{-1}$ have been obtained (Table 8) (59).

In different experimental conditions the quantum yields for this reaction with TCPO can be considerable lower, as shown by the values obtained in a tetrahydrofuran (THF)/water mixture using DPA, perylene and RUB as ACT (Table 8) (148). With *N,N'*-bis(tosyl)-1H,4H-quinoxaline-2,3-dione (TsQD) instead of TCPO as substrate, considerably higher quantum yields were obtained in the same conditions, although these yields were still much lower than the ones obtained in anhydrous medium (Table 8) (148).

A detailed study on the peroxyoxalate reaction using different oxalic esters as substrates and substituted distyrylbenzenes (**19**) as

ACT in a THF water mixture (3:1) with sodium carbonate was performed (Table 8) (149). The quantum yields proved to depend on the nature of the substrate as well as on the electronic properties of the substituents on the distyrylbenzene ACT. Although oxalic esters with more electron attracting substituents are expected to possess higher quantum yields, this is not observed with the esters studied. However, this unexpected fact can be explained by the occurrence of hydrolysis reactions in the aqueous medium, reducing the quantum efficiency of more reactive derivatives. In addition, quantum yields are generally higher for derivatives of **19** with electron-donating substituents, indicating the occurrence of an electron transfer from the ACT to the HEI formed in the reaction according to the CIEEL mechanism (Table 8) (149).



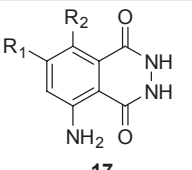
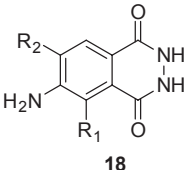
CONCLUSION

The present compilation of quantum yields for several CL transformations allows the following general conclusions:

1. The unimolecular decomposition of cyclic peroxides occurs with low CL quantum yields due to the fact that mainly triplet excited states are formed in this process, which are essentially nonemissive. Therefore, these transformations are not adequate models for efficient BL.
2. The catalyzed decomposition of cyclic peroxides, like diphenoyl peroxide and 1,2-dioxetanones, leads to preferential formation of singlet excited states having, however, relatively low quantum yields, as shown by recent quantum yield re-determinations. Therefore, these transformations also cannot be regarded as adequate models for efficient BL.
3. The induced decomposition of phenoxy-substituted 1,2-dioxetanes occurs with the involvement of an intramolecular electron transfer and a vast number of examples for this transformation with extremely high quantum yields has been reported. Therefore, this transformation constitutes an adequate model for efficient BL.
4. The luminol oxidation in a variety of experimental conditions occurs with quantum yields of 0.01–0.02 $E \text{ mol}^{-1}$ in aqueous medium and this reaction is one of the most adequate for the calibration of CL emission detection instruments due to its simplicity and availability, being utilized by many research groups. Although the mechanism of the luminol reaction has not been fully understood, chemiexcitation might involve an intramolecular electron transfer in a cyclic peroxide intermediate.
5. The peroxyoxalate reaction is one of the most efficient CL transformations known, as testified by quantum yield determinations performed by different research groups. As this reaction has been shown to proceed by an intermolecular electron transfer, according to the CIEEL mechanism, it constitutes the only example for this transformation with proven high quantum yields.

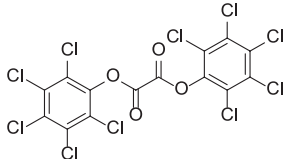
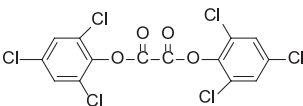
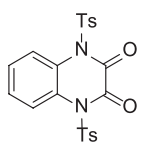
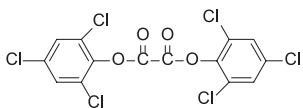
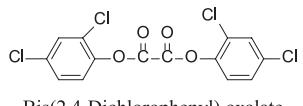
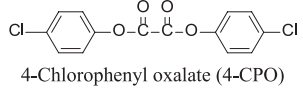
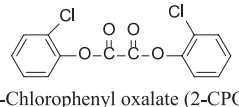
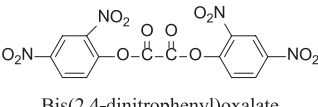
The final conclusion reached from the data and discussions above is that electron transfer processes are of outstanding importance in the chemical formation of electronically excited states and that intramolecular processes (CIEEL intra) are highly

Table 7. Quantum yields of the reaction of luminol and isoluminol derivatives with hemin and hydrogen peroxide.

Compound	Φ_{CL} ($E \text{ mol}^{-1}$)
 <p>17</p>	<p>17a: R₁ = H; R₂ = H 0.015 17b: R₁ = H; R₂ = CH₃ 0.028 17c: R₁ = H; R₂ = CH₃CH₂CH₂ 0.017 17d: R₁ = H; R₂ = CH₃CHCH₃ 0.012 17e: R₁ = H; R₂ = CH₃OCH₂ 0.006 17f: R₁ = (CH₃)₃C; R₂ = H 0.012</p>
 <p>18</p>	<p>18a: R₁ = H; R₂ = H 0.0012 18b: R₁ = H; R₂ = CH₃ 0.0011 18c: R₁ = CH₃; R₂ = H 0.0006</p>

Quantum yields obtained using the luminol standard ($\Phi_{CL} = 0.0125 E \text{ mol}^{-1}$) (94).

Table 8. Quantum yields ($E \text{ mol}^{-1}$) for the peroxyoxalate reaction with different oxalic derivatives and activators.

Reagent	$\Phi_{\text{CL}} \times 10^2$	$\Phi_{\text{S}} \times 10^2$	ACT	Method ^{a,b}	Ref.
 Bis(pentachlorophenyl) oxalate (PCPO)	15	15.8	DPA	IV / A	(60)
 Bis(2,4,6-trichlorophenyl) oxalate (TCPO)	5.7 ± 0.8	6.0 ± 0.8	DPA	III / B	(59)
	67 ± 5	68 ± 5	rubrene	III / C	
	0.0023	0.0023	DPA		
	0.029	0.030	perylene	V / D	(148)
 N,N'-bis(tosyl)-1H,4H-quinoxaline-2,3-dione (TsQD)	0.053	0.054	rubrene		
	0.047	0.047	DPA		
	0.27	0.29	perylene	V / E	
	0.67	0.68	rubrene		
	0.72	*	19a		(148)
	0.21	*	19b		
	0.058	*	19c	V / F	
 Bis(2,4,6-trichlorophenyl) oxalate (TCPO)	0.0069	*	19d		
	0.011	*	19b		
	0.0033	*	19c		
	0.0011	*	19d		
 Bis(2,4-Dichlorophenyl) oxalate (2,4-DCPO)	0.0027	*	19e		
	0.063	*	19b		
	0.015	*	19c		
	0.0025	*	19d		
 4-Chlorophenyl oxalate (4-CPO)	0.010	*	19e		
	0.036	*	19b		
	0.0062	*	19c	V / G	(149)
	0.0015	*	19d		
 2-Chlorophenyl oxalate (2-CPO)	0.005	*	19e		
	0.087	*	19b		
	0.018	*	19c		
	0.0041	*	19d		
 Bis(2,4-dinitrophenyl)oxalate (DNPO)	0.016	*	19e		
	0.011	*	19b		
	0.0017	*	19c		
	0.0004	*	19d		
	0.0011	*	19e		

efficient, whereas intermolecular transformations (CIEEL inter) possess low efficiency. For an understanding of the general factors which regulate the efficiency of CL transformations it appears of outstanding interest to rationalize the difference in efficiency of inter and intramolecular CIEEL processes and to understand the reasons for the exceptionally high efficiency of the peroxyoxalate reaction occurring by an intermolecular CIEEL mechanism.

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Table 8. (continued)

*Calibration methods: III – modified luminol standard (59) IV – absolute calibration, (60) V – luminol standard (94); †Conditions: A: [PCPO] = 5×10^{-4} mol L⁻¹, [H₂O₂] = 5×10^{-5} mol L⁻¹, [sodium salicylate] = 1.2×10^{-4} mol L⁻¹, [DPA] = 5×10^{-3} mol L⁻¹ in chlorobenzene; B: [TCPO] = 10^{-3} mol L⁻¹, [H₂O₂] = 10^{-2} mol L⁻¹, [imidazole] = 10^{-3} mol L⁻¹, DPA in ethyl acetate, 25°C, value obtained by extrapolation to infinite activator concentrations; C: [TCPO] = 10^{-3} mol L⁻¹, [H₂O₂] = 10^{-2} mol L⁻¹, [imidazole] = 10^{-3} mol L⁻¹, rubrene in ethyl acetate, 25°C, value obtained by extrapolation to infinite activator concentrations; D: [TCPO] = 5.0×10^{-6} mol L⁻¹, [H₂O₂] = 1.5×10^{-1} mol L⁻¹, [ACT] = 1.4×10^{-4} mol L⁻¹ in THF/H₂O; E: [TsQD] = 5.0×10^{-6} mol L⁻¹, [H₂O₂] = 1.5×10^{-1} mol L⁻¹, [ACT] = 1.4×10^{-4} mol L⁻¹ in THF/H₂O; F: [TsQD] = 1.0×10^{-5} mol L⁻¹, [19] = 2.0×10^{-4} mol L⁻¹, [H₂O₂] = 3.0×10^{-1} mol L⁻¹ in THF/H₂O; G: [oxalic ester] = 3.8×10^{-6} mol L⁻¹, [19] = 7.5×10^{-6} mol L⁻¹, [H₂O₂] = 2.5×10^{-3} mol L⁻¹, [Na₂CO₃] = 7.5×10^{-5} mol L⁻¹ in THF/H₂O 3:1; ‡Singlet quantum yields not determined.

SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Table S1. Quantum yields ($E \text{ mol}^{-1}$) for the decomposition of additional examples of 1,2-dioxetane derivatives containing aromatic hydroxyl groups initiated by deprotonation.

Table S2. Quantum yields ($E \text{ mol}^{-1}$) for the decomposition of some additional examples of 1,2-dioxetane derivatives containing silyl-protected aromatic hydroxyl groups, induced by fluoride deprotection.

Detailed procedures for determination of chemiluminescence quantum yields: (i) Calibration according to the Hastings-Weber Procedure; (ii) Calibration with the modified luminol standard; (iii) Calibration relative to 3-adamantylidene-4-(3-*tert*-butyl-dimethylsiloxyphenyl)-4-methoxy-1,2-dioxetane.

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