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Singlet-Oxygen Chemiluminescence in Peroxide Reactions

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1. Introduction

The process of transforming chemical energy into light emission, a phenomenon known as chemiluminescence (CL), has been an attractive topic of intensive research over the years, in view of its fundamental mechanistic significance and the diversity of practical applications.[1−12] The in-depth knowledge of chemiluminescent systems paves the way for understanding the otherwise difficult to explore “dark” processes associated with such reactions. This is well illustrated, for instance, by the discovery of the quantum-chain reactions (with and without energy branching) through the detailed elucidation of the CL affiliated with the thermal decomposition of dioxetanes.[13−17]

Among the various known chemiluminescent reactions, the intervention of singlet oxygen ($^1O_2$) is of particular interest in the context of the present review. Since its spectral detection in the early 1960s,[18−25] the singlet-oxygen CL has been extensively studied, especially during the last few decades, once ultrasensitive detectors became available[26−28] in the late 1970s to monitor faint light emission in solution. This rapidly expanding field of research is of fundamental concern in biology,[29] chemistry, environmental and material sciences, and medicine. As shall be illustrated below, the $^1O_2$ CL has been often invoked to account for the light emission in chemical and biological processes. Evidently, numerous analytical applications in chemistry and biology rest on our ample understanding of the CL exposed by singlet oxygen.

Various aspects of singlet-oxygen chemistry have been intensively reviewed. The numerous reviews and monographs published to date[30−61] in this field have been mainly concerned with the photophysical properties and photobiological involvement of $^1O_2$ (modes of generation, pathways of deactivation, damage of living matter, toxicity, and mechanisms of quenching). Moreover, the role of $^1O_2$ as an oxidant in organic synthesis and its intermediacy as a reactive intermediate in biochemistry has been extensively reviewed. In contrast, the $^1O_2$ CL in peroxide reactions (the major chemical source of singlet oxygen) has been considered only occasionally.[30−32,37,39,61] Such mention mainly concentrated on the well-known hydrogen peroxide/ hypochlorite (or Cl_2) chemiluminescent system (Scheme 1); indeed, this is the chemical process in which singlet-oxygen CL was first discovered.[18−25] Since its discovery, numerous new peroxide-based chemiluminescent systems have been reported, in which singlet oxygen participates as the key light emitter; however, this relevant and significant subject matter in CL has to date not been reviewed. The incentive of the present literature survey is to fill this gap and provide an overview of the important role that $^1O_2$ plays in the field of peroxide CL. In such chemiluminescent peroxide systems, either singlet oxygen acts as the direct emitter or it constitutes the oxidant to mediate light emission, presumably through an intermediary dioxetane.

The numerous light-generating systems are presented and their mechanisms are scrutinized. Briefly, also the advantages of the CL method for singlet-

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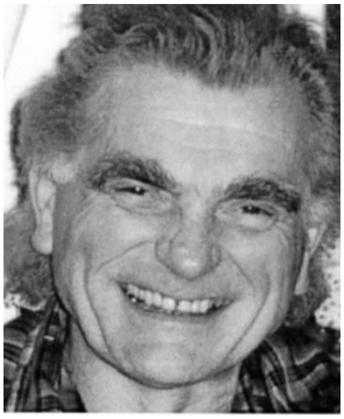
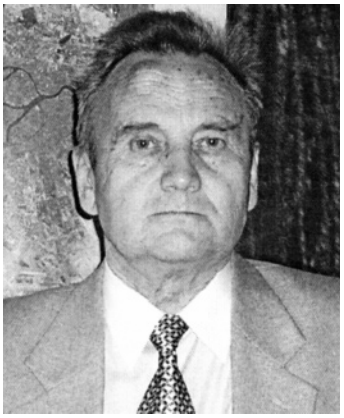


Waldemar Adam was born in 1937, in Alexanderdorf, Ukraine. He received his B.Sc. in 1958 from the University of Illinois and his Ph.D. from MIT (with F. D. Greene) in 1961. He was appointed Assistant Professor at the University of Puerto Rico in 1961 and was promoted to Associate Professor in 1965 and to Professor in 1970. Since 1980 he occupied the Chair of Organic Chemistry at the University of Würzburg and served as Co-Director of the Institute of Organic Chemistry. Currently, he holds a part-time appointment at the Department of Chemistry of the University of Puerto Rico, Rio Piedras, after having been retired by the University of Wuerzburg in October 2002. His manifold research interests encompass mechanistic organic chemistry, with an emphasis on peroxides, singlet oxygen, photochemistry, photobiology, chemiluminescence and bioluminescence, and synthetic and biomedical applications of metal-catalyzed and enzyme-catalyzed oxidation chemistry. He has received numerous national and international awards for his research work, which now encompasses over 970 publications.

Dmitri V. Kazakov was born in Ufa, Russia, in 1970. He received his degree in chemistry in 1993 from the Bashkirian State University and Ph.D. in physical chemistry in 1997 from the Institute of Organic Chemistry of the Russian Academy of Sciences in Ufa. He joined Professor Valeri Kazakov's Laboratory in 1997, where he currently works as a senior research associate. In 2000-2002, he joined Professor Adam's group at University of Würzburg as a DAAD and Alexander-von-Humboldt postdoctoral fellow to work on the generation of singlet oxygen from dioxirane reactions. Chemiluminescence of high-energy peroxides, with emphasis on dioxiranes and singlet oxygen, oxidative chemiluminescence, and its mechanisms, and energy transfer processes are among his major scientific interests. His research activity was marked by various awards and fellowships intended for young scientists, including European Academy Prize received in 1999.



Valeri P. Kazakov was born in Vladimiro-Alexandrovskoe, Russia, in 1934. He received his degree in chemistry from the University of Sankt-Petersburg (former Leningrad) in 1957 on radiochemistry as a specialization. He was then engaged in the study of scintillation methods for detection of ^{14}C (radiocarbon) and later (1960–1968) in the investigation of the thermodynamics of complex formation with participation of d-elements at the Institute of Inorganic Chemistry of the Siberian Branch of Academy of Sciences of USSR (Novosibirsk). Since 1971 he has been a Head of the Laboratory of Chemical Physics at the Institute of Organic Chemistry of the Russian Academy of Sciences in Ufa (Russia). From 1987 to 1993, he served as a vice-president of the Ufa Scientific Center of the RAS. In 1990, he was selected as a corresponding member of the Russian Academy of Sciences. His research interests range from the photochemistry, radiochemistry, and radiothermoluminescence of frozen solutions and polymers, to the chemiluminescence of metals of the d and f elements, which includes uranium and lanthanide complexes, as well as the chemistry and chemiluminescence of energy-rich organic peroxides and xenon compounds. He is coauthor of more than 400 articles and 6 monographs.

oxygen detection and quantification are addressed. Our focus shall deal with reactions, in which the singlet oxygen has been originally generated in the liquid phase, although in some cases the light emission occurs from a gas bubble, as manifested in the aqueous $ClO^-{-}H_2O_2$ system. The numerous gas-phase processes, particular in atmospheric chemistry, are beyond the scope of this review; furthermore, the $^1O_2$ emission in photochemical pathways will also not be considered since the emphasis herein is on peroxide reactions.

Scheme 1

$$H_2O_2 + {}^-OCl \longrightarrow O_2 + H_2O + Cl^- + h\nu$$

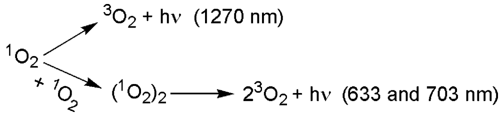
2. Singlet-Oxygen Monomol and Dimol Emissions

The historical background of singlet-oxygen CL has been extensively described by Khan and Kasha[39,61,62] and shall not be covered here, except for the ClO^- (or Cl_2)/H_2O_2 reaction (Scheme 1). The latter constitutes a fundamental case of singlet-oxygen generation in a peroxide reaction, which is of significance and relevance in the context of the present review because it provides the characteristic spectral fingerprint for the intermediacy of singlet oxygen.[18,20−25]

The first publication of CL derived from the reaction of ClO^- with H_2O_2 was reported as far back as in 1913,[63] but the development of the field proceeded rather slowly.[63−67] The breakthrough came in the 1960s when the involvement of singlet oxygen was confirmed spectroscopically in the CL of hypohalite and related reactions.[18−25,62,68−72] These findings paved the way for the development of the phenomenon of singlet-oxygen emission, generated chemically in peroxide reactions, as witnessed by the intensive research activities that ensued in the numerous branches of $^1O_2$ chemistry. It was shown that the observed CL is caused by monomeric singlet oxygen (monomol emission) and its dimeric aggregate ($[^1O_2]_2$, dimol emission), as shown in Scheme 2.

The spectral characteristics of these emitting excited states ($^1\Sigma_g{}^+$ and $^1\Delta_g$) derived from singlet

Scheme 2



oxygen, which have been recorded[18,20,22,24,25,62,72,73] for the hypochlorite (or Cl_2) reaction with hydrogen peroxide, are summarized in Scheme 3; the principal emission bands fall in the visible (Vis) and infrared (IR) spectral regions. In addition to the emissions listed in Scheme 3, the fluorescent $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ transition at 1925 nm also has been recorded[57,74−78] in the photosensitized generation of singlet oxygen, whereas an attempt to observe it in a chemical reaction failed.[74] Moreover, of all the bands in Scheme 3, only the emissions in the visible region at 633 and 703 nm for $(^1O_2)_2$ and the infrared emission at 1270 nm (the emission maximum may be slightly shifted by the solvent[58,79,80]) for the $^1\Delta_g$ state of $^1O_2$ are regularly observed in singlet-oxygen CL reactions.

Scheme 3

$^1O_2$:

1580 nm: $(0,1)\ ^1\Delta_g \longrightarrow {}^3\Sigma_g^-$

1270 nm: $(0,0)\ ^1\Delta_g \longrightarrow {}^3\Sigma_g^-$

1070 nm: $(1,0)\ ^1\Delta_g \longrightarrow {}^3\Sigma_g^-$

865 nm: $(0,1)\ ^1\Sigma_g^+ \longrightarrow {}^3\Sigma_g^-$

770 nm: $(1,1)\ ^1\Sigma_g^+ \longrightarrow {}^3\Sigma_g^-$

762 nm: $(0,0)\ ^1\Sigma_g^+ \longrightarrow {}^3\Sigma_g^-$

$(^1O_2)_2$:

786 nm: $(^1\Delta_g)_{v=0}(^1\Delta_g)_{v=0} \longrightarrow (^3\Sigma_g^-)_{v=2}(^3\Sigma_g^-)_{v=0}$

703 nm: $(^1\Delta_g)_{v=0}(^1\Delta_g)_{v=0} \longrightarrow (^3\Sigma_g^-)_{v=1}(^3\Sigma_g^-)_{v=0}$

633 nm: $(^1\Delta_g)_{v=0}(^1\Delta_g)_{v=0} \longrightarrow (^3\Sigma_g^-)_{v=0}(^3\Sigma_g^-)_{v=0}$

578 nm: $(^1\Delta_g)_{v=1}(^1\Delta_g)_{v=0} \longrightarrow (^3\Sigma_g^-)_{v=0}(^3\Sigma_g^-)_{v=0}$

477 nm: $(^1\Sigma_g^+)_{v=0}(^1\Delta_g)_{v=0} \longrightarrow (^3\Sigma_g^-)_{v=0}(^3\Sigma_g^-)_{v=0}$

381 nm: $(^1\Sigma_g^+)_{v=0}(^1\Sigma_g^+)_{v=0} \longrightarrow (^3\Sigma_g^-)_{v=0}(^3\Sigma_g^-)_{v=0}$

The numerous physicochemical aspects (radiative and nonradiative deactivation rate constants, lifetimes, solvent effects, quenching mechanisms, etc.) of the $^1\Delta_g$ and $^1\Sigma_g^+$ states of singlet oxygen have been recently reviewed in detail by Schmidt and Schweitzer[58] and will only be briefly mentioned herein.

The first excited state of molecular oxygen, namely, $^1\Delta_g$, has been intensively investigated for nearly 45 years. Traditionally, it is referred to as *singlet oxygen* to distinguish it from the triplet ground state of dioxygen, which lies 22.5 kcal/mol lower in energy. Even in solution, the $^1\Delta_g$ state possesses a rather long lifetime, which depends significantly[58,81] on the solvent (e.g., the lifetime is as much as 59 ms in CCl_4 but only ca. 3.1 μs in H_2O). Nevertheless, even in water, in which singlet oxygen is shortest lived, the lifetime is still long enough for detecting the emission by its infrared CL. The IR−CL intensity may also be affected by quenchers[41,81] such as amines, phenols, or alcohols, which may be present during the chemical generation. The properties of the second excited state of molecular oxygen, namely, the $^1\Sigma_g^+$ state (in energy 37.5 kcal/mol above $^3O_2$), have been extensively explored only in recent decades. The $^1\Sigma_g^+$ state has a very short lifetime in solution, which is several orders of magnitude lower than that of the $^1\Delta_g$ state. Since the $^1\Sigma_g^+$ state is rapidly and efficiently deactivated to the $^1\Delta_g$ state, it does not contribute significantly to the $^1O_2$ emission in peroxide reactions. Thus, it is $^1O_2$ ($^1\Delta_g$) that will be the light-emitting species in the chemiluminescent peroxide systems described herein.

In contrast to the well-developed chemistry of the $^1\Delta_g$ state of singlet oxygen, the dimer aggregate $(^1O_2)_2$ remains to date still a relatively unexplored species. Despite the rather long history[18−25] of the singlet-oxygen dimol emission, the chemistry behind this phenomenon is as yet not well understood. Most of the present-day knowledge on the dimol structures does not come from chemiluminescent but rather from the photosensitized studies on singlet oxygen. Thus, it is known that the dimol and monomol singlet-oxygen species are in equilibrium with one another, as shown in Scheme 4. The dissociation rate constant k_{dis} of the dimol entity has been estimated to lie in the 10^{10}−10^{12} s^{-1} range.[82−86] For instance, the k_{dis} values in CS_2 and in CCl_4 (the lower limit of k_{dis}) have been reported to be 3.3×10^{11} s^{-1} and 2.6×10^{10} s^{-1}, and, consequently, the dimol species has a lifetime (τ) in the picosecond range,[82,85,87] specifically, 3 ps in CS_2 [82] and 38 ps in CCl_4.[85] Furthermore, recently an upper limit for the radiative decay rate constant (k_d) of $(^1O_2)_2$ in $CDCl_3$ has been determined[86] to be $(1.2 \pm 0.3) \times 10^3$ s^{-1}, which is larger than the k_d values in the gas phase[87] and argon matrix.[88] This implies that the k_d parameter should also be sensitive to the type of solvent; however, no detailed solvent-dependent studies on the k_d values have been carried out to date. To be noted is the finding that the radiative rate constant estimated[86] for $(^1O_2)_2$ is larger than that reported[58,89−91] for $^1O_2(^1\Delta_g)$. Furthermore, it has been shown that the dimol luminescence intensity at 580, 633, and 703 nm (gas phase) depends on temperature.[92] Additionally, Chou et al.[84] noticed that the integrated intensity ratio of the dimol emission bands for the 0,0 (633 nm) versus 0,1 (703 nm) transitions in CCl_4 solution depends on the triplet-oxygen concentration. It was suggested[84] that triplet oxygen may interact with the $(^1O_2)_2$ collisional pair.

Scheme 4

$$^1O_2 + {}^1O_2 \underset{k_{dis}}{\overset{k_{assoc}}{\rightleftharpoons}} (^1O_2)_2 \longrightarrow {}^3O_2 + {}^3O_2 + h\nu$$

Important results on the properties of the dimol species have been furnished by Deneke and Krinsky,[93,94] who found that the CL at 633 and 703 nm of the H_2O_2−ClO^- system increased in the presence of

1,4-diazabicyclo[2.2.2]octane (DABCO). A similar observation has been subsequently made by Sies et al.[95] Kanofsky suggested[96] that DABCO causes this enhancement effect because of the increased rate of $^1O_2$ production; however, Sies and Di Mascio have shown[97] that besides the hypochlorite/H_2O_2 system DABCO also enhances the dimol emission at 703 nm that is generated in the thermal decomposition of disodium 3,3′-(1,4-naphthylidene)dipropionate endoperoxide. Neither the kinetics of the endoperoxide decomposition nor the singlet-oxygen yields of the endoperoxide and of the $H_2O_2-ClO^-$ system were influenced by DABCO. Later, Krasnovsky et al.[98] observed a similar effect in their photosensitized studies, namely, that the $(^1O_2)_2$ emission at 703 nm increased when photosensitizers such as *pheophytin a*, *pheophorbide a*, 2,3,7,8-dibenzopyrene-1,6-quinone, or tetraphenylporphine were used. This perplexing phenomenon of the dimol-CL enhancement needs still to be explained.

The CL-enhancement effect by DABCO is, however, not general, since it was recently shown[99] that DABCO efficiently quenches the CL of the dimol species, generated in the decomposition of 1,4-dimethylnaphthalene endoperoxide, in the ketone-catalyzed breakdown of $KHSO_5$, as well as in the reaction of dioxiranes with tertiary amines and nucleophilic anions. These results[99] should caution us not to regard DABCO as a reliable probe for the detection of $(^1O_2)_2$ in peroxide-type chemiluminescent systems.

3. Quantification of Singlet Oxygen by Means of Chemiluminescence

The discovery of the monomol and dimol emissions from singlet oxygen[18−28,68−73] has made available spectroscopic methods for the detection and quantification of singlet oxygen (mostly through the characteristic IR−CL at λ 1270 nm) in chemical as well as in biological processes (see refs 100−121). In some cases, the IR−CL was useful to detect $^1O_2$ when other detection modes such as chemical trapping failed. This is well illustrated by the chemiluminescent reactions of hydrogen peroxide with CH_3CN,[114] in which $^1O_2$ is produced.

The characteristic $^1O_2$ IR−CL not only allows one to detect singlet oxygen but also to quantify it. The essence of the method is to compare the $^1O_2$ IR−CL emission of the reaction in question with that of a standard reaction, whose singlet-oxygen yield is known. As a convenient peroxide reaction for such a calibration standard, we recommend the decomposition of the triphenyl phosphite ozonide and of the 1,4-naphthalene endoperoxide, the reaction of H_2O_2 with ClO^- or N-chlorosuccinimide, and the catalyzed decomposition of hydrogen peroxide by molybdate ions. All these have been successfully used for the quantification of singlet oxygen by the IR−CL method.[103,116−121] It should be emphasized that more reliable results are obtained when the reaction in question is carried out in the same solvent as that of the standard reaction. If this is not the case, then corrections for the different radiative and nonradiative rate constants of the singlet-oxygen decay in these distinct solvents should be made.

Unquestionably, the IR−CL method is the most convenient for the detection and quantification of singlet oxygen; however, older methods, e.g., chemical trapping, are still being employed for this purpose. For instance, in reactions in which $^1O_2$ is only slowly produced and strongly deactivated by the solvent (e.g., H_2O), the IR−CL signal is too weak to be detected spectroscopically, such that chemical trapping is the analytic method of choice. Nevertheless, it must be cautioned that chemical traps do not only react with $^1O_2$, but they also may be oxidized by the peroxide source of singlet oxygen or any other oxidative species generated in the peroxide reaction. For instance, hydrotrioxides may react with the singlet-oxygen acceptor, such that the $^1O_2$ yield is seriously overestimated by the chemical method. A prominent example of such a discrepancy is the use of benzaldehyde hydrotrioxide as $^1O_2$ source: A singlet-oxygen yield as high as 96% has been measured in the chemical trapping experiments,[122] whereas by the spectroscopic IR−CL method[118] it was only 0.4%! Moreover, chemical acceptors may physically quench the singlet oxygen and thereby falsify the results of the measurements. In addition, the use of the direct IR−CL method avoids tedious isolation adduct and its quantification of the $^1O_2$. Sometimes such isolation is cumbersome, in particular for labile singlet-oxygen adducts such as the endoperoxides of aromatic hydrocarbons. Finally, the spectroscopic monitoring of the $^1O_2$ IR−CL also provides a useful tool for measuring singlet-oxygen quenching rate constants, as well as for conducting kinetic studies.[114,115,121,123−127]

4. Prototypes of Chemiluminescent Peroxide Reactions

With the characteristic spectral features of the monomol and dimol emissions of singlet oxygen discussed and the detection and quantification of $^1O_2$ by the IR−CL method on hand, we now present the various distinct peroxide chemiluminescent systems as prototypes, in which singlet oxygen figures as the emitting species. An overview of such chemiluminescent transformations to be covered in this review is summarized in Figure 1, conveniently presented by means of a rosette in the chronological order as they appear in the text. We shall commence with the thermal decomposition of endoperoxides (transformation 1), continue with the base-catalyzed reactions of hydrogen peroxide (transformation 2), and cover the numerous cases of metal peroxo complexes which generate singlet oxygen on thermolysis (transformation 3). The catalyzed breakdown of dioxiranes (transformation 4) and peroxy acids (transformation 5) are given next, followed by the thermal decomposition of trioxides and phosphine ozonides (transformation 6). Next comes the generation of singlet oxygen from tetraoxides, produced by the recombination of peroxyl radicals according to the Russell mechanism (transformation 7), and from the interaction of ozone (transformation 8) and superoxide ion (transformation 9) with a variety of organic and inorganic substances. The rosette terminates with the reaction of peroxynitrites with hydrogen peroxide and hydroperoxides (transformation 10), and the base-induced

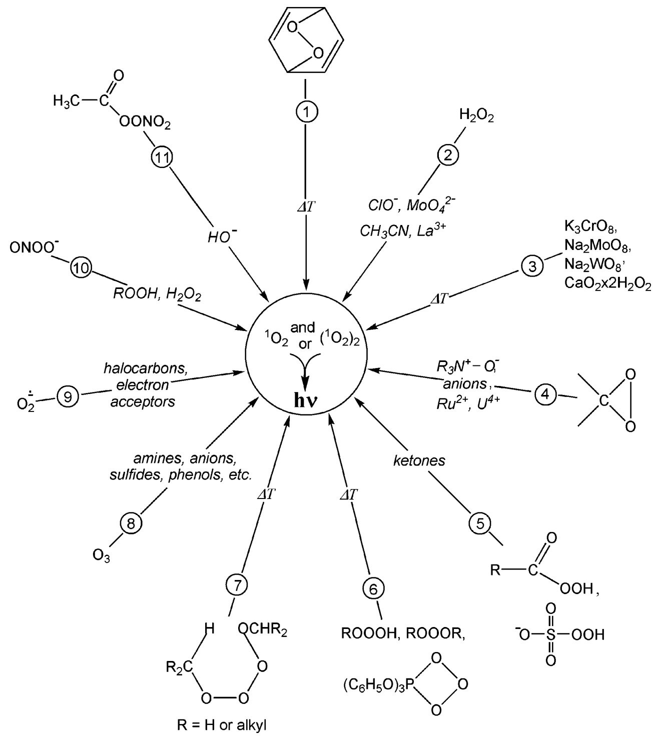


Figure 1. Overview of singlet-oxygen CL in peroxide reactions.

decomposition of peroxyacetyl nitrate (transformation 11).

Conspicuous is the diversity of peroxide reactions in which electronically excited molecular oxygen is formed, and unusual is the high efficiency of the excited-state generation. Indeed, as may be seen from Table 1, sometimes the $^1O_2$ is produced even quantitatively (!), such that these chemiluminescent processes are among the most efficient ones known to afford excited species. Unfortunately as yet no general theory exists to predict the excitation efficiency of a chemiluminescent reaction; however, some qualitative requisites must be fulfilled[6,11] for such a process to generate excited states at all and, hence, emit light. The pertinent ones for $^1O_2$ are listed briefly:

(i) The *energy sufficiency* criterion must be fulfilled, the most important requisite, which demands that the sum of the reaction heat (ΔH_r) and activation energy ($\Delta H^{\ddagger}$) be greater than, or at least equal to, the energy of the excited-state product (Figure 2). The $^1\Delta_g$ state of molecular oxygen possesses only 22.5 kcal/mol, so that it may be excited in rather low exothermic reaction; indeed, excitation may also take place even during an endothermic process, provided that the activation energy is high enough to reach $^1\Delta_g$ level of O_2.

(ii) The *structure resemblance* criterion must apply, which requires that the structure of the activated complex should resemble that of the excited state to be formed. In most peroxide reactions that release $^1O_2$, the R−O bonds in the R−O−O−R functionality are cleaved, such that the activated complex [$(R\cdots O{-}O\cdots R)^{\ddagger}$] is structurally similar to the incipient $^1O_2$ molecule.

As should be evident, these two general conditions for chemiluminescent reactions are well fulfilled in the generation of electronically excited molecular oxygen. Consequently, it is not surprising that $^1O_2$ is essentially ubiquitously and even quantitatively formed in so many peroxide reactions. But there exists an electronic feature, specific for $^1O_2$, which additionally promotes excited-state generation, namely, the distinct spin configurations of $^1O_2$ versus $^3O_2$. The spin-conservation rule, a quantum-mechan-

Table 1. Singlet-Oxygen Yields in Representative Peroxide Reactions

peroxide reaction	yield (%)	method[a]	medium[b]	ref
hydrogen peroxide with				
hypochlorous acid	100	chem trap	water	128
MoO_4^{2-}	100	chem trap[c]	water	129, 130
N-chlorosuccinimide	100	chem trap	water	131
CH_3CN	100	IR−CL	water	114
decomposition of endoperoxides				
1,4-dimethylnaphthalene	76	chem trap	organic	132
1,4-dimethoxy-9,10-diphenylanthracene	95	chem trap	organic	132
3,3′-(1,4-naphthylidene)dipropionate	51	chem trap	water	97
decomposition of peroxo complexes				
Na_2MoO_8, Na_2WO_8	160[d]	IR−CL chem trap	water	116
DMD[e] and TFD[f] with				
Cl^-, Br^-, $O_2^{\bullet-}$	30−100	IR−CL	organic	133
decomposition of ozonides				
$(PhO)_3PO_3$	100	chem trap	organic	134
peroxymonosulfuric acid				
decomposition	100	chem trap	water	135
with acetone	100	IR−CL	water	124
ozone with				
R_2S, RSSR, $MeSO_2H$, NO_2^-	100	IR−CL	water	121
R_3N, Br^-	56−90	IR−CL	water	

[a] Chemical traps used in organic medium: 9,10-dimethylanthracene, tetracyclone, rubrene, tetraphenylcyclopentadienone, 9,10-diphenylanthracene; in water: 2,5-dimethylfuran, tetrapotassium rubrene-2,3,8,9-tetracarboxylate, cesium and sodium anthracene-9,10-bis(ethanesulfonate), sodium 9,10-bis(2-ethylene)anthracene disulfate. [b] Organic solvents used: 1,4-dioxane, $CHCl_3$ (for endoperoxides), CH_2Cl_2, acetone, $CH_2Cl_2{-}CCl_4$, acetone-CH_3CN (for dioxiranes), CH_2Cl_2 (for $(PhO)_3PO_3$). [c] Results of chemical trapping have been also confirmed by the IR−CL method (ref 123). [d] On the basis of peroxy complexes. [e] DMD, dimethyldioxirane, [f] TFD, methyl(trifluoromethyl)dioxirane.

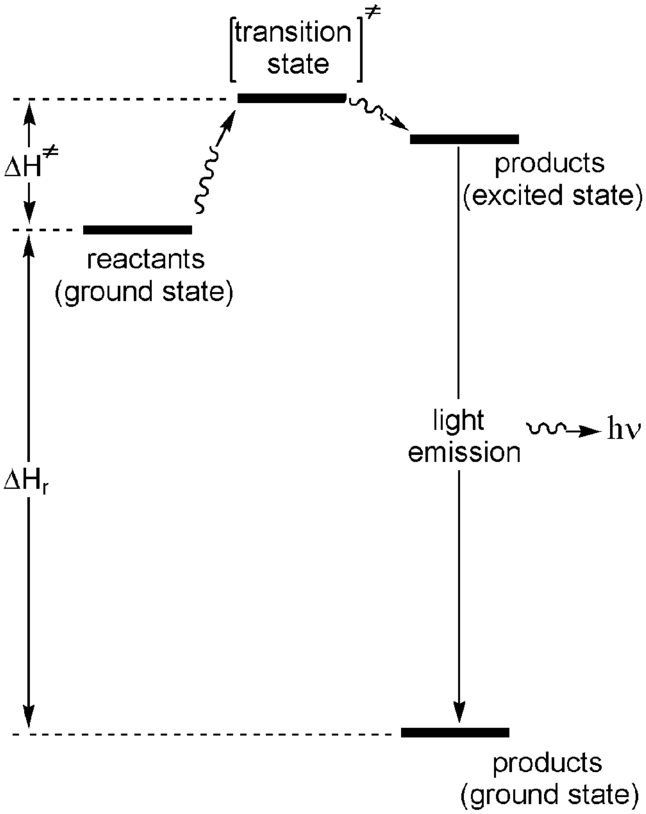


Figure 2. Energy profile for a general chemiluminescent reaction; $\Delta H^{\ddagger}$ is the activation energy and ΔH_r is the reaction heat.

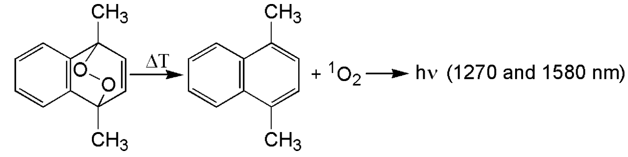
ical imposition, dictates that the spin-paired peroxide precursor liberates molecular oxygen in its singlet state, necessarily the electronically excited $^1O_2$.

In the next subsections, we elaborate in detail the qualitative and quantitative studies of peroxide reactions that generate $^1O_2$. It must be emphasized that in most of the presented examples, the spectroscopic detection has been indispensable in verifying the authenticity of the singlet-oxygen intervention.

4.1 Endoperoxides

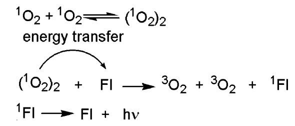
In the thermal decomposition of endoperoxides, rather high yields of singlet oxygen are produced (Table 1),[132,136] as manifested initially by the chemical trapping experiments and later by the more reliable CL techniques. For instance, the infrared emission occurs at the maxima 1580[137] and 1270[74,138] nm for the decomposition of 1,4-dimethylnaphthalene endoperoxide in carbon tetrachloride (Scheme 5), which are associated with 0,1 and 0,0 transitions ($^1\Delta_g \rightarrow {}^3\Sigma_g^-$) of $^1O_2$. The 1270-nm emission has also been recorded in the thermolysis of 1,4-dimethoxy-9,10-diphenylanthracene[137] and 3,3′-(1,4-naphthylidene)-dipropionate[97,139] endoperoxides. Furthermore and mechanistically significant, the formation of the singlet oxygen in the 1,4-endoperoxide thermolysis constitutes a rather unusual case, since the excited state is formed in an endothermic process and requires thermal activation energy for the reaction to occur.[132,136]

Scheme 5



The intriguing aspect of the endoperoxide CL concerns the emission in the visible spectral range, which is observed[97,138,140−143] along with IR−CL emission. A particular case constitutes the decomposition of the 1,4-dimethylnaphthalene endoperoxide[138,140] or the 3,3′-(1,4-naphthylidene)dipropionate endoperoxide,[97] in which the observed Vis−CL has been attributed to the singlet-oxygen dimol emission. There are, however, some reports in which the fluorescence from the regenerated parent hydrocarbon has been claimed as, for example, during the thermolysis of the 1,4-dimethoxy-9,10-diphenylanthracene endoperoxide.[141,142] In the case of the 1,4-dimethoxy-9,10-dipyridylanthracene endoperoxide, both the hydrocarbon fluorescence (λ_{max} 480 nm) and the dimol emission (beyond 610 nm) have been documented.[143] These light emissions display different kinetics: The intensity at 480 nm increases, whereas that beyond 610 nm decreases as the reaction proceeds. The 480-nm emission has been proposed[143] to involve energy transfer from the singlet-oxygen dimol ($^1\Sigma_g^+, {}^1\Delta_g$) to the hydrocarbon. This energy-transfer mechanism was later invoked by Fu, Foote, and Krasnovsky[138] to explain the tetra-*tert*-butylphthalocyanine emission during the thermolysis of 1,4-dimethylnaphthalene endoperoxide in the presence of this dyestuff. The explanation is based on the hypothesis first suggested by Khan and Kasha[25] that light may be generated by direct energy transfer from an excited molecular-oxygen pair (the dimol species) to a suitable fluorescing acceptor (Fl), as shown in Scheme 6.

Scheme 6



The energy-transfer process of the singlet-oxygen dimol has been under intensive mechanistic dispute for almost four decades,[5,25,82,98,138,143−158] that is, since its conception in 1966.[25] Besides in endoperoxide CL, it also has been proposed for other organic and inorganic (salts of f and d elements[5]) fluoresers, sensitized by the $^1O_2$ generated chemically or photochemically[98,138,143,144,146,147,149,151,152,156] (Scheme 6). Nonetheless, alternatives to the dimol mechanism have also been suggested, namely, the direct energy transfer from $^1O_2$ to form a fluorescer triplet,[144,145,147,153−155] or the involvement of a $^1O_2$-acceptor exciplex,[146,153] followed by excitation with another $^1O_2$ molecule to afford the singlet-excited emitter.

4.2 Hydrogen Peroxide

The reaction of hydrogen peroxide with hypochlorite (Scheme 1) has made a major impact on the singlet-oxygen CL field. Since its discovery, this reaction has been studied in detail[128,159−161] and has been used as a model system for efficient (almost quantitative under appropriate conditions[128,161]) generation of singlet oxygen (Table 1). Moreover, the ClO^-/H_2O_2 system has been applied as a source of gaseous $^1O_2$ to feed powerful chemical iodine laser.[46,162]

Initially it was affirmed that the singlet-oxygen CL of the hypochlorite/hydrogen peroxide reaction in solution actually stems from singlet-oxygen molecules trapped in gas bubbles;[62] in later studies, however, it was shown that visible and infrared CL also may be observed[163,164] from the bulk solution; however, the naked human eye perceives only the red dimol emission, which supposedly occurs in the oxygen gas phase.

An unusual claim about the $ClO^-{-}H_2O_2$ CL was made by Brabham and Kasha,[150] who observed CL at λ_{max} 813 nm from the methylene blue and other thiazine dyes, when these were present in the reaction of ClO^- with hydrogen peroxide. The authors proposed[150] involvement of the sigma state ($^1\Sigma_g^+$) of singlet oxygen to explain the emission by the thiazine dye, namely, through the energy transfer from this singlet-oxygen state to the triplet-excited dye. Scurlock and Ogilby[82] also pointed out the possibility of such a dye excitation, since the $^1\Sigma_g^+$ state is formed in solution by means of energy pooling with the $^1\Delta_g$ state.[82]

The IR−CL emission from singlet oxygen at 1270 nm was observed[165] in the chloride-ion-catalyzed decomposition of hydrogen peroxide under acidic conditions, in which hypochlorous acid is formed[166,167] in situ by the oxidation of the chloride ion. Even the decomposition of hydrogen peroxide in alkaline aqueous medium is accompanied by weak CL.[168] From the spectral analysis of the emission bands (478, 634, and 703 nm) as well as the influence of the deuterated water on the luminescence intensity, this CL was assigned[168] to the singlet-oxygen dimol.

The metal-catalyzed decomposition of hydrogen peroxide is known to produce singlet oxygen in rather high yields.[129] Singlet-oxygen CL has been later recorded in some of these catalytic reactions. Specifically, Brauer and Böhme reported[123] the IR−CL emission of $^1O_2$ at 1270 nm in the catalyzed decomposition of H_2O_2 by molybdate ions in aqueous media at pH 10.5 (Scheme 7). Recently, the IR−CL of singlet oxygen in the MoO_4^{2-}-catalyzed decomposition of hydrogen peroxide has been also recorded in organic solvents.[169] The IR−CL measurements[123] have confirmed an earlier study by Aubry and Casin,[129,130] that singlet oxygen is generated in high efficiency in the MoO_4^{2-}/H_2O_2 system (Table 1). Formation of $^1O_2$ may occur by the decomposition of both MoO_6^{2-} and MoO_8^- formed by the reaction of the molybdate ion with H_2O_2 (Scheme 7); however, it was shown[123] that the decomposition of MoO_8^{2-} does not significantly contribute to $^1O_2$ formation; the latter occurs mainly[123] in the decomposition of the diperoxo species MoO_6^{2-} (Scheme 8). The diperoxo intermediate is generated in the Na_2MoO_8 decomposition, the process that is also accompanied by IR−CL of $^1O_2$, as was shown by Niu and Foote.[116] Besides the peroxomolybdates MoO_8^{2-}, peroxytungstates WO_8^{2-} also are able to produce $^1O_2$ with high efficiency (Table 1) during their thermal decomposition in basic aqueous solution, as shown in Scheme 9.[116] Moreover, the decomposition of dimeric tetraperoxy species $M_2O_{11}^{2-}$ under alkaline conditions also gives rise to IR−CL emission by singlet oxygen.[116]

Scheme 7

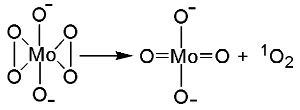
$$MoO_4^{2-} + 2H_2O_2 \rightleftharpoons MoO_6^{2-} + 2H_2O$$

$$MoO_6^{2-} \longrightarrow MoO_4^{2-} + {}^1O_2$$

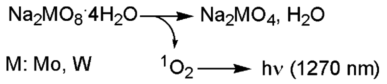
$$MoO_6^{2-} + 2H_2O_2 \rightleftharpoons MoO_8^{2-} + 2H_2O$$

$$MoO_8^{2-} \longrightarrow MoO_6^{2-} + {}^1O_2$$

Scheme 8



Scheme 9



Notably, the first observation of the IR−CL of $^1O_2$ in the breakdown of metal peroxocomplexes has been made by Pitts and co-workers,[170,171] who recorded the 1270-nm emission during the decomposition of the potassium perchromate in aqueous solution (Scheme 10). The $^1O_2$-releasing potassium perchromate is readily formed by the reaction of the chromate ion with H_2O_2 under alkaline conditions; indeed, the emission of $^1O_2$ at 1270 nm is also observed[170,171] in its in situ decomposition. In contrast to peroxomolybdate and peroxotungstate decomposition, the perchromate reaction in Scheme 10 affords only 6% of singlet oxygen.[171] Quite recently, a new peroxo complex, namely, the calcium peroxide diperoxohydrate ($CaO_2 \times 2H_2O_2$), has been reported[172] to produce the 1270-nm emission of $^1O_2$ (yield is 25%) upon decomposition. The IR−CL emission of singlet oxygen at 1270 nm was also detected in the V^{5+}-catalyzed decomposition of H_2O_2 in acetic acid,[173] presumably through the intermediary diperoxo species. Similarly, singlet-oxygen infrared CL was produced in the catalyzed disproportionation of hydrogen peroxide by lanthanum(III) ions under heterogeneous conditions.[174]

Scheme 10

$$K_3CrO_8 \xrightarrow{H_2O} {}^1O_2$$

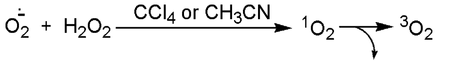
The Vis−CL emission observed[175,176] during the reaction of hydrogen peroxide with Fe^{2+} (Fenton's reagent) and by ferricyanide $Fe(CN)_6^{3-}$ occurs at a shorter wavelength than that characteristic for $(^1O_2)_2$. Nevertheless, the dimol emission of $^1O_2$ was shown[177−179] to play a role in the reactions related to the $Fe^{2+}{-}H_2O_2$ system, e.g., in the peroxidation of linoleic acid,[177] initiated by the reaction of ferrous ion with H_2O_2.

In the $Eu^{2+}-H_2O_2$ system, which is similar to the Fenton reaction, the emissions at λ_{max} 580 and 630 nm have as well been attributed[180] to the singlet-oxygen dimol species. In addition to these singlet-oxygen emissions, CL from the Eu^{3+} ion, formed by the H_2O_2 oxidation, has been observed.[180] When coronand ligands are used for the europium metal, a more complex chemiluminescent scenario ensues, in which the emission near λ_{max} 500 nm is attributed to excited carbonyl fragments.[180] In the presence of a ligand azide (N_3^-)[181] or polyamino acids,[182] the Eu^{3+} CL of the Eu^{2+}/H_2O_2 system was attributed to the energy transfer from the $^1O_2$ dimol to the Eu^{3+} ion.

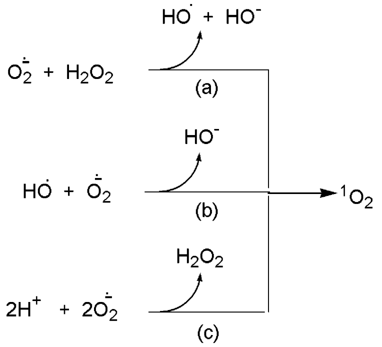
The decomposition of hydrogen peroxide in basic media in the presence of the Eu^{3+}/thenoyltrifluoroacetone (TTA) complex leads to europium ion CL around 600 nm.[183] Excitation of the Eu^{3+} chelate was proposed to occur by energy transfer from the products (in particular, singlet oxygen) of the H_2O_2 decomposition. It should be stressed, however, that the involvement of singlet oxygen in these oxidative systems[180−183] has not been experimentally validated.

The interaction of the superoxide ion with hydrogen peroxide in either carbon tetrachloride or acetonitrile was shown[184] to be chemiluminescent (Scheme 11). The three steps in Scheme 12 have been proposed[184] to account for the singlet-oxygen CL: The Haber-Weiss reaction (path a), the electron transfer between the hydroxyl radical and the superoxide ion (path b), and the dismutation of the superoxide ion (path c).

Scheme 11



Scheme 12



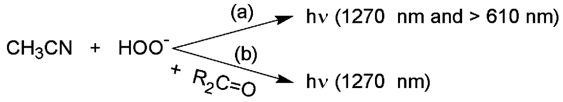
The CL of the singlet-oxygen dimol species has as well been observed[185] (Scheme 13) in the reaction of nitric oxide with H_2O_2. The same CL was reported[185] for the reaction of NO• with other peroxides, e.g., butyl and cumene hydroperoxides.

Scheme 13

$$H_2O_2 + NO^{\cdot} \xrightarrow{pH\ 7 - 7.4} h\nu\ (633 \text{ and } 703 \text{ nm})$$

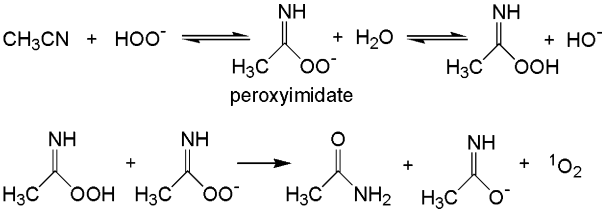
Although the formation of the singlet oxygen in the reaction of alkaline hydrogen peroxide with acetonitrile has been a contradictory issue,[186−188] the observation of IR−CL at 1270 nm has convincingly proved[114] that singlet oxygen is generated, in fact, quantitatively (Table 1). Moreover, this reaction is accompanied[189] by the emission of red light (λ > 610 nm), which was attributed to the $^1O_2$ dimol as the emitter (Scheme 14, path a). The mechanism in Scheme 15 has been proposed[114] to explain the production of $^1O_2$ in the HOO^-/CH_3CN system. The key step responsible for the singlet-oxygen CL is the reaction of the peroxyimidate ion with the corresponding peroxy acid.

Scheme 14



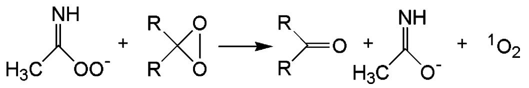
R_2CO: acetone, *N,N*-dimethyl-4-oxo-piperidinium nitrate

Scheme 15



When ketones are introduced into the HOO^--CH_3CN system (Scheme 14, path b), the IR−CL intensity at 1270 nm is significantly enhanced, presumably through the in situ formation of a dioxirane, which releases $^1O_2$ by the reaction with the peroxyimidate (Scheme 16).[114] This is in analogy to the well-established mechanism for the ketone-catalyzed decomposition of peroxy acids (see Section 4.5). Additional support for the intermediary dioxirane in this reaction provides the study by Shu and Shi,[190] who demonstrated that the $HOO^-/CH_3CN/R_2CO$ system possesses efficient epoxidation power, a characteristic reactivity of dioxiranes.

Scheme 16

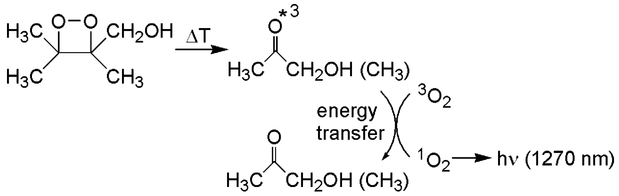


In some enzymatic reactions (lactoperoxidase, catalase, and chloroperoxidase)[100] of hydrogen peroxide, as well as in the oxidation of organic compounds[115,116,165,191−196] by H_2O_2, CL has been observed in the IR and visible regions, which derives from singlet oxygen. For instance, the oxidation of formaldehyde and some polyphenols by alkaline H_2O_2 is accompanied by Vis−CL[191−194,196] due to the singlet-oxygen dimol, whereas the interaction of hydrogen peroxide with the *p*-nitrophenyl chloroformate,[165] *p*-nitrophenyl 1*H*-1,2,4-triazolecarboxylate,[115] *N,N′*-carbonyldi-1,2,4-triazole,[115] or *N*-chlorosuccinimide[116] displays IR−CL at 1270 nm due to the $^1O_2$ monomol.

4.3 Dioxetanes

The generation of singlet oxygen was reported[197] during the thermal decomposition of 3-hydroxymethyl-3,4,4-trimethyl-1,2-dioxetane, a four-membered-ring cyclic peroxide, as detected by the accompanying IR−CL at 1270 nm. The thermolysis of such a dioxetane leads to triplet-excited ketone, which by energy transfer to molecular oxygen affords $^1O_2$, as shown in the mechanism in Scheme 17.

Scheme 17

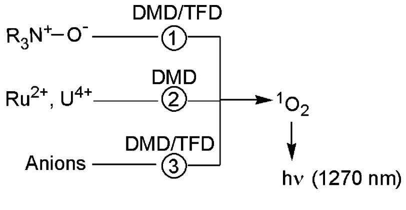


Although the singlet-oxygen yield is low (ca. 0.1%), this work[197] illustrates that $^1O_2$ may be produced by energy transfer to molecular oxygen from the electronically excited ketones that are generated in the chemical systems. Historically significant, as far back as 1964 the possibility was suggested that excited singlet oxygen may be produced by the energy transfer from excited carbonyl products, the latter formed in the decay of organic peroxides.[198] Later, such an energy-transfer process has been invoked for several chemiluminescent reactions, e.g., in the recombination of peroxyl radicals, the decomposition of trioxides, and the oxidation of diphenyldiazomethane, which shall all be considered below.

4.4 Dioxiranes

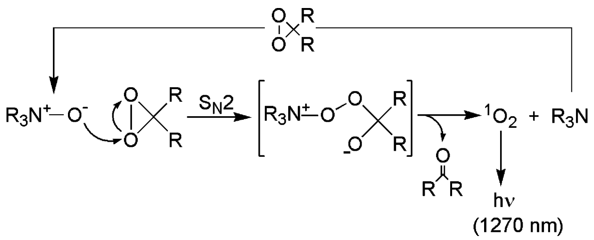
Dioxiranes, three-membered-ring peroxides, are known as highly efficient and selective oxidants capable of performing a variety of oxidative transformations valuable for synthetic purposes.[199−205] It was recently shown that some of these chemical transformations are accompanied by CL due to the release of singlet oxygen. In particular, the CL of singlet oxygen at 1270 nm was observed in the *N*-oxide-catalyzed decomposition[117,206,207] (Scheme 18, pathway 1) of dimethyldioxirane (DMD) and methyl(trifluoromethyl)dioxirane (TFD), in the metal-induced reaction[208−210] of DMD (Scheme 18, pathway 2), and in the catalyzed[133,207,211] decomposition of DMD and TFD by anionic nucleophiles (Scheme 18, pathway 3).

Scheme 18



The mechanism in Scheme 19 was proposed[117,206] to explain the singlet-oxygen formation for the reaction of *N*-oxides with dioxiranes. It starts with the nucleophilic attack by the negatively charged *N*-oxide oxygen atom on the dioxirane peroxide bond with formation of a dipolar *N*-oxide-dioxirane adduct, followed by heterolytic cleavage of the latter into singlet oxygen, ketone and amine. Finally, the released amine is then again oxidized by another dioxirane molecule to complete the catalytic cycle.

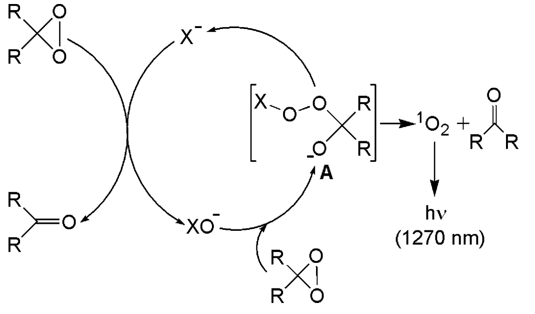
Scheme 19



The efficiency of the singlet-oxygen production (0.1−30%)[117] depends on the structure of the amine and on whether DMD or TFD is employed. For example, the most effective amine is 4-(dimethylamino)pyridine, for which the singlet-oxygen yield in the reaction with DMD is ca. 30%. Moreover, no DMD decomposition and, consequently, no IR−CL of $^1O_2$ is obtained for the nonnucleophilic pyridine and pyridine-type heteroarenes,[117] whereas these amines still promote the decomposition of TFD with release of $^1O_2$ (up to 5% yield). For the 4-dimethylaminopyridin-*N*-oxide, besides the IR emission at 1270 nm, visible CL of the singlet-oxygen dimol at 630 and 703 nm was recorded.[99,206]

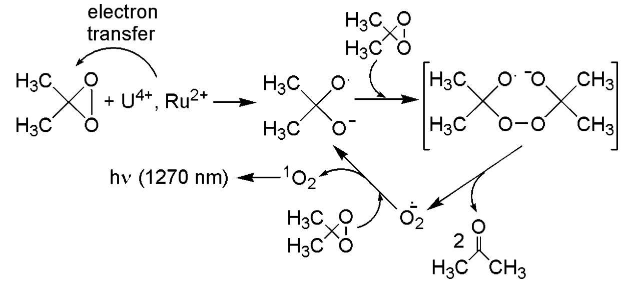
A similar mechanism (Scheme 20) has been proposed[133,207,211] to account for the formation of singlet oxygen during the catalytic decomposition of dioxiranes by nucleophilic anions X^- (Cl^-, Br^-, I^-, $O_2^{\bullet-}$, OH^- and t-BuO^-). For the single-electron-donating superoxide and iodide ions, alternatively the mechanism of electron-transfer chain decomposition[212] operates to release the singlet oxygen in the dioxirane decay.[133] This electron-transfer mechanism is more likely to occur for TFD, which is more readily reduced than DMD. Nevertheless, in analogy to the iodide-catalyzed breakdown of TFD,[212] an electron-transfer chain decomposition of DMD has been suggested to account for the $^1O_2$ CL at 1270 nm, emitted during the reaction of the dioxirane with uranium(IV) ions in acidic aqueous acetone solutions[210] and also with the tris(bipyridine)ruthenium(II) complex,[208,209] as shown in Scheme 21. According to this mechanism, electron transfer to DMD leads to the DMD radical anion, which then reacts with another DMD molecule by nucleophilic attack on the peroxide bond to afford the dimeric radical anion. To complete the catalytic cycle, the superoxide ion transfers an electron to DMD to produce the singlet oxygen and regenerate another dioxirane radical anion.

Scheme 20



In the reaction of the Ru^{2+} and U^{4+} ions with DMD, not only is IR−CL emitted by $^1O_2$ but also visible light

Scheme 21



is emitted.[208-210] Whereas in the case of U^{4+} ions, the emitter of the Vis−CL at λ_{max} 510−540 nm is not known;[210] for the Ru^{2+} it was found[208,209] that the emitter at λ_{max} 615 nm is the Ru^{2+} species. The formation of the excited Ru^{2+} has been attributed[208,209] to the chemically induced electron exchange luminescence (CIEEL)[213-215] mechanism.

Vis−CL is also found[99,133,211] in the reaction of DMD with chloride, bromide, and iodide ions. The spectral appearance of this CL for the reaction of the peroxide with chloride ion is rather complex and consists of five bands at 380−450, 450−510, 510−550, 550−600, and 600−650 nm. In addition, the emission at 700 nm was recorded by means of interference filters. It was suggested,[99,133,211] however, that the emission at λ > 560 nm, as well as that at 700 nm, belongs to the singlet-oxygen dimol species.

Rather high yields of $^1O_2$ (Table 1) have been recorded for the reaction of dioxiranes with nucleopilic anions (e.g., ca. 100% for the chloride ion).[133,211] The solvent influence on the Vis−CL emission provided additional support for the involvement of the $^1O_2$ dimol species.[99,133] Thus, the CL intensity at λ > 600 nm for the reactions of DMD with the chloride ion in a water−acetone mixture is significantly lower than in halogenated solvents,[99,133] which is caused by the reduced singlet-oxygen lifetime in aqueous acetone.[58] Likewise, the more than 2-fold decrease in the Vis−CL intensity a 700 nm (interference filter) found[99,133] for the reaction of the dioxirane with both the bromide and the chloride ions in a CCl_4−acetone (1:1) or a CCl_4−CH_2Cl_2 (1:1) mixture, compared to pure carbon tetrachloride, is a consequence of the lower $^1O_2$ lifetime in acetone and methylene chloride versus carbon tetrachloride.

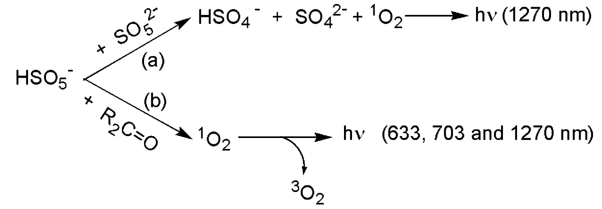
Dioxiranes are also key intermediates responsible for singlet-oxygen CL in the ketone-catalyzed decomposition of peroxy acids, as shall be addressed next (Section 4.5).

4.5 Peroxy Acids

Monoperoxysulfuric acid (Caro's acid) is known to decompose under alkaline conditions in aqueous solution into sulfuric acid and molecular oxygen;[135,216,217] the latter is generated in its singlet excited state, as evidenced by chemical trapping experiments (Table 1).[135] Brauer and Lange[124] definitively confirmed this chemical generation of singlet oxygen by recording IR−CL at 1270 nm (Scheme 22, path a).

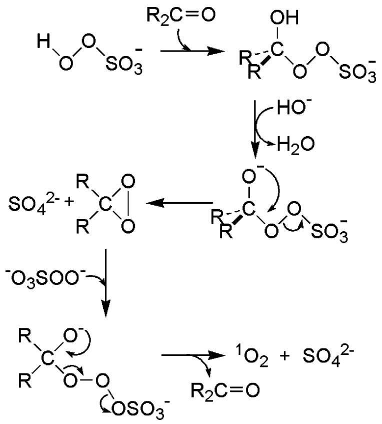
Ketones such as acetone, butanone, and cyclohexanone catalyze efficiently the decomposition of the Caro acid and, consequently, enhance substantially the IR−CL intensity.[124,218] The acetone-catalyzed decomposition of Caro acid is also accompanied by the emission in the visible spectral region,[99] with λ_{max} at 633 and 703 nm due to the formation of the singlet-oxygen dimol (Scheme 22, path b).

Scheme 22



The above-mentioned ketone-catalyzed[219] decomposition of Caro's acid is the main synthetic route to dioxiranes,[220,221] whose mechanism (Scheme 23) has been elucidated in detail.[222] In this mechanism, the nucleophilic attack by the monopersulfate ion on the peroxide bond of the intermediary dioxirane is the key step responsible for the formation of singlet oxygen. The resulting trioxide derivative fragments heterolytically into singlet oxygen and the sulfate ion, with regeneration of the ketone. A similar mechanism has been suggested[223] to explain the IR−CL emission of $^1O_2$ at 1270 nm during the ketone-catalyzed decomposition of monoperoxyphthalic, monoperoxymaleic, peroxyacetic, and *m*-chloroperoxybenzoic acids.

Scheme 23

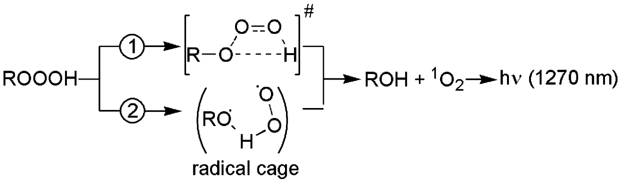


4.6 Trioxides

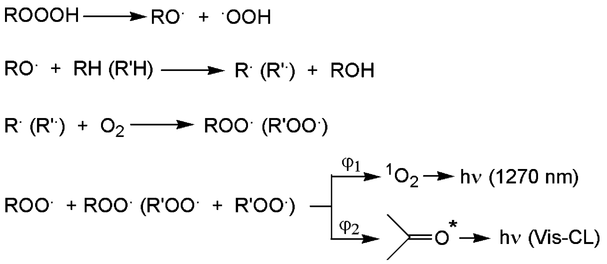
The trioxides,[122,224-229] namely, hydrotrioxides ROOOH and the dialkyl trioxides ROOOR, as well as the ozonides [e.g., phospite ozonides $(RO)_3PO_3$)][134] are rather labile species, which must be handled at low temperature. Their thermal decomposition produces singlet oxygen, as manifested by CL. Thus, the IR−CL (λ > 1000 nm) and Vis−CL (λ = 400−500 nm) emissions have been recorded[230,231] during the release of molecular oxygen from the breakdown of the organic trioxides $CH_3CH_2CH(OH)OOOH$, $(CH_3)_2C(OH)OOOH$, $CH_3CH_2C(OH)(CH_3)OOOH$, and $C_6H_5C(O)OOOH$. Subsequently, a diversity of hydrotrioxides has been shown[118,232-236] to emit IR−CL and Vis−CL. The IR−CL at 1270 nm derives in all cases from singlet oxygen, while for the CL in the visible spectral region the electronically excited carbonyl products are held responsible, which are formed during the hydrotrioxide decomposition. In addition to the 1270-nm emission, the triethylsilyl[232] and benzaldehyde[233] hydrotrioxides afford the 1580-nm emission from the 0,1 ($^1\Delta_g \rightarrow {}^3\Sigma_g^-$) transition of $^1O_2$.

The mechanism of the radiative hydrotrioxide decomposition depends on the trioxide structure and on the experimental conditions (temperature and solvent).[228] The pathway 1, depicted in Scheme 24, proceeds through a concerted transition state, whereas in pathway 2 a caged radical pair intervenes. In Scheme 25, alternatively, a radical-chain process operates, in which the singlet oxygen is generated by the Russell mechanism through the recombination of two peroxyl radicals ROO$^\bullet$ (to be considered in detail in the next section). The source of the precursor radical for the peroxyl species is either the solvent (R′H) or the parent hydrocarbon (RH), provided the trioxide synthesis has been carried out in such media. Quenching of the excited carbonyl products by triplet oxygen (Scheme 26) as a channel of singlet-oxygen production may be excluded,[231] since the quantum yield of $^1O_2$ excitation (φ_1) is much higher[231] than the efficiency of generating excited carbonyl states (φ_2). The most likely pathway for the formation of electronically excited carbonyl products, which emit in the visible spectral region, entails radical-chain decomposition,[228,234] namely, during the recombination of peroxyl radicals (Scheme 25).

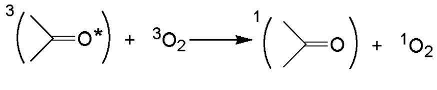
Scheme 24



Scheme 25

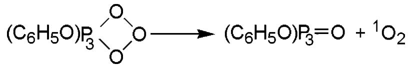


Scheme 26



The related ozonides also emit CL upon decomposition.[119,125,237–239] For instance, the IR−CL emission has been ascribed[119,237] to the singlet oxygen generated during the thermal decay of triphenyl phosphite ozonide $(PhO)_3PO_3$ (Scheme 27), which is known to produce $^1O_2$ quantitatively (Table 1). Additionally, also the Vis−CL emission at 400−600 nm has been observed,[237] which may be enhanced by the strongly fluorescing 9,10-dibromoanthracene and 9,10-diphenylanthracene, and attributed[237] to the triplet-excited triphenyl phosphate product. Kinetically interesting, the time profile of the Vis−CL decay is complex and differs significantly from the characteristic first-order decay of the IR−CL.[237] It was suggested that presumably small quantities (not detectable by NMR) of other labile peroxides are formed during the ozonide synthesis, which on decomposition produce excited carbonyl species that excite the triphenyl phosphate by energy transfer. Recent work confirms[239] that an unknown excited species is generated during the decomposition of solid triphenyl phosphite ozonide and during its thermal decomposition in solution. This is manifested by observation of a broad background emission around the 634- and 703-nm peaks; the latter emissions belong presumably to that from the $(^1O_2)_2$ species.

Scheme 27



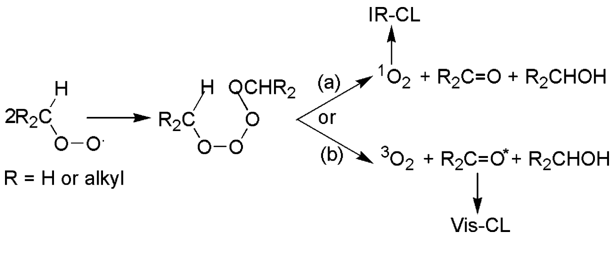
The Vis−CL emission observed in the thermolysis of 1-phospha-2,8,9-trioxaadamantane ozonide was attributed[240] to the singlet-oxygen dimol species; however, the detailed spectral study of this chemiluminescent process has not been carried out to substantiate this tentative claim. Finally, even the simple metal ozonides KO_3 and NaO_3 give rise[241] to singlet-oxygen IR−CL emission during their decomposition in water.

4.7 Tetraoxides through the Recombination of Peroxyl Radicals

4.7.1 Primary and Secondary Peroxyl Radicals

A tetraoxide intermediate is proposed to be formed in the recombination[242−244] of peroxyl radicals (the Russell termination), which is a common termination step in many chemical and biological autoxidation processes.[120,245] During the decomposition of this labile intermediate, the singlet oxygen is generated as shown in Scheme 28 (pathway a). The spectroscopic manifestation of the formation of the singlet oxygen in such autoxidation of hydrocarbons and radical-induced decomposition of hydroperoxides rests on the IR−CL of $^1O_2$ at 1270 nm (Scheme 28).[119,120,245,246] Azoalkanes, hyponitrites, and redox-active transition-metal ions (e.g., the ceric ion) have been employed for the radical initiation. Notably, in the ceric-ion-induced decomposition of ethyl hydroperoxide (a source of primary peroxyl radicals), a longer wavelength IR−CL emission also was noted,[120] which is not characteristic for singlet oxygen. Presumably, the unknown emitter derives from side reactions of $^1O_2$.[120]

Scheme 28



In addition to the IR−CL, the highly exothermic peroxy-radical recombination is also accompanied by CL in the visible spectral region,[247−252] in which carbonyl products are the emitting species (Scheme 28, pathway b). This visible CL is enhanced by appropriate activators, for which most commonly anthracene derivatives and europium complexes have been employed. The efficiency of CL enhancement depends on the nature of activator used, namely, whether triplet-energy or singlet-energy acceptors are used. Actual measurements have revealed that the efficiency of triplet formation in the peroxyl-radical recombination is several orders of magnitude higher than that of singlet states.[247−252] The singlet-oxygen yield in the recombination of secondary and primary peroxyl radicals is relatively low and averages only about 8%,[119,120,246] as quantified by the IR−CL method. The quantum efficiency of $^1O_2$ production is essentially independent of the radical structure, with the exception of substrates that bear a heteroatom near the peroxyl group, which may lower the $^1O_2$ yield.[119]

The mechanism in Scheme 28 accounts adequately for the singlet-oxygen generation from such a peroxyl-radical self-reaction.[119,120,243] Alternatively,[119,120,253] it may be envisaged that the $^1O_2$ could be produced by energy transfer from the intermediary excited triplet ketone to ground-state oxygen, as shown in Scheme 29; however, this energy-transfer mechanism in the tetraoxide decomposition seems to be unlikely on the grounds of efficiency considerations:[119,246] The yield of $^1O_2$ production[119,120,246] in pathway a of Scheme 28 is significantly higher (ca. 8%) than the triplet yield ($<1\%$)[247−252] of excited carbonyl species formed in pathway b.

Scheme 29

$$R_1R_2CHOOOOCHR_1R_2 \longrightarrow {}^3[R_1R_2CO^*] + {}^3O_2 \longrightarrow R_1R_2CO + {}^1O_2$$

The mechanistic possibility has been raised[119,246,253] that the singlet oxygen may be initially generated in the ($^1\Sigma_g^+$) state during the tetraoxide decomposition and subsequently rapidly decays[57,58] to its $^1\Delta_g$ state, which is spectroscopically detected by its IR−CL emission. The observation[254] of the CL for the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ transition during the self-reaction of alkylperoxy radicals in the gas-phase lends circumstantial spectral support for this hypothesis. Experimental confirmation of the $^1O_2$ ($^1\Sigma_g^+$) involvement during the tetraoxide decomposition in the solution phase will certainly be difficult. In this connection, it is relevant to cite the work of Chou and Frei,[74] who failed to detect the $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ emission at 1930 nm during the photoinduced decay of 1,4-dimethylnaphthalene endoperoxide, despite the fact that the generation of the $^1O_2$ ($^1\Sigma_g^+$) state from an excited aromatic endoperoxide has been theoretically predicted.[255,256]

Also the bimol emission of singlet oxygen has been invoked in the self-reaction of peroxyl radicals. For example, the CL at $\lambda > 570$ nm that has been recorded[245] in the recombination of secondary peroxyl radicals during the radical-induced decomposition of the hydroperoxide derived from linoleic acid has been attributed[245] spectrally to the bimol $(^1O_2)_2$ emission. Similarily,[257] the rather complex CL emission detected at 470−640 nm, which arises from the radical-induced decomposition of secondary peroxyl radicals, was also assigned to the ($^1\Sigma_g$),($^1\Delta g$) and ($^1\Delta g$),($^1\Delta g$) transitions of the singlet-oxygen dimol intermediate.

4.7.2 Tertiary Peroxyl Radicals

The chemiluminescent reaction in Scheme 28 cannot apply for tertiary peroxyl radicals; nevertheless, the IR−CL emission of singlet oxygen was observed[120] in a $^1O_2$ yield of up to 2% in the decomposition of *tert*-butyl hydroperoxide and cumyl hydroperoxide, induced by ceric ammonium nitrate. Two possibilities have been proposed to explain this observation mechanistically: The first one entails the direct formation of $^1O_2$ according to Scheme 30,[120] whereas in the second one[119,120] the tertiary alkoxyl radicals fragments into methyl radicals, which then react with molecular oxygen to form methylperoxyl radicals and subsequent self- or cross-termination (Scheme 28) leads to singlet oxygen. Mechanistically pertinent in this context is the fact that the oxidation of tertiary hydrocarbons also produces weak CL emission in the visible spectral region due to the emission from triplet-excited carbonyl products.[258]

Scheme 30

$$R_3COOOOCR_3 \longrightarrow R_3COOCR_3 + {}^1O_2$$

5. Miscellaneous Reactions

5.1 Ozone

Ozone-induced CL has been known for more than a hundred years.[259] In recent decades, it was shown that singlet oxygen is the emitter in some ozone chemiluminescent reactions. Various substrates, also biomolecules, have been shown to produce IR−CL of $^1O_2$ in their liquid[102,103,121] and gas-phase[260] reactions with ozone (Scheme 31). Most of these processes are accompanied[102,103,121] by rather high yields of $^1O_2$ (Table 1).

Scheme 31

$$O_3 + S \longrightarrow {}^1O_2 \longrightarrow h\nu \text{ (1270 nm)}$$

S: amines, sulfur-containing compounds, phenols, DNA constituents, nucleophilic anions (NO_2^-, N_3^-, Br^-, I^-, CN^-), cysteine, methionine, albumin, uric acid, etc.

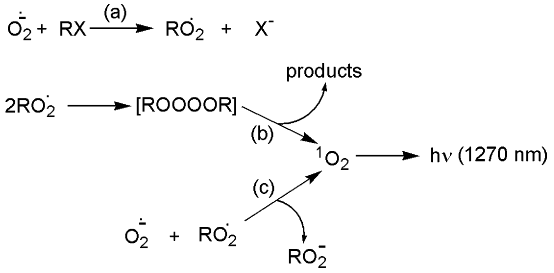
Excited molecular oxygen has been invoked to explain the CL in the visible spectral region during the reaction of ozone with ClO_2 [261] and in the decomposition of ozone at a glass surface in concentrated sulfuric acid solutions.[262,263] Introduction of UO_2^{2+} or Tb^{3+} and Dy^{3+} ions into these systems leads to the excitation of the metals ions, presumably by energy transfer from singlet-oxygen dimol species or higher excited states of $^1O_2$.[5] Moreover, the IR−CL emission of $^1O_2$ was also detected[264] during the ozone decomposition in CCl_4, suspended with silica gel. Recently, the IR CL of singlet oxygen has been reported[265] in the reaction of ozone with tin(II) ions in acetic acid or with nitrite ions in water.

5.2 Superoxide Ion

Khan has reported[39,266] the singlet-oxygen IR−CL for the reaction of $O_2^{\bullet-}$ with a number of electron acceptors, such as lead tetraacetate, bis(cyclopentadienyl)titanium dichloride, ceric ammonium nitrate, and bis(cyclopentadienyl) ferricenium hexafluorophosphate. The rather complex emission spectra in the visible region during the reaction of the thianthrene cation radical perchlorate with the superoxide ion was also ascribed to singlet-oxygen CL.[267]

The characteristic IR−CL of $^1O_2$ was reported[268,269] during the interaction of the superoxide ion with water in halogenated solvents. It was suggested,[163,270,271] however, that this IR−CL was not caused by water, but instead by the reaction[272] of $O_2^{\bullet-}$ with the halocarbons. For example, the halocarbons CCl_4, CBr_4, $C_6H_5CCl_3$, C_4H_9Br, and $CHCl_3$ produce[270,271] IR−CL of $^1O_2$ in the reaction with the superoxide ion, whereas visible emission is observed during the interaction of $O_2^{\bullet-}$ with CCl_4, $CHCl_3$, $C_2H_4Br_2$, decachlorobiphenyl, and 2,3,7,8-tetrachlorodibenzo-*para*-dioxin.[273] For the singlet-oxygen formation, the mechanism in Scheme 32 was proposed,[270,271] in which the initially formed peroxyl radicals recombine (pathways a and b), according to Russell termination, as described in Section 4.7, but also an electron-transfer reaction may operate (pathway c). Finally, the addition of the benzoyl peroxide to the KO_2-(18-crown-6)-$CHCl_3$ system increases[270] significantly the IR−CL intensity, which confirms the claim[274] that the $^1O_2$ is produced in the reaction of superoxide with diacyl peroxides.

Scheme 32



X: Cl or Br

5.3 Peroxynitrite

Monomol and dimol light emissions of singlet oxygen have been observed[275−277] during the reaction of peroxynitrite with hydrogen peroxide, as well as with *tert*-butyl hydroperoxide and linoleic acid (LA) hydroperoxide[277] (Scheme 33). Similarly, the singlet-oxygen CL may also be expected in the ketone-catalyzed decomposition of peroxynitrites. Indeed, the $^1O_2$ formation was predicted in this case as a result of the reaction of $ONOO^-$ with an intermediary dioxirane.[278]

Scheme 33

$$ONOO^- + H_2O_2\ (t\text{-BuOOH and LAOOH}) \longrightarrow h\nu\ (>610\ \text{nm and } 1270\ \text{nm})$$

The claim as to whether the peroxynitirite decomposition in aqueous solution produces singlet oxygen is controversial.[279−282] Khan et al. have reported[279,280] the IR−CL emission of $^1O_2$ during the decomposition of the peroxynitrite after protonation (Scheme 34), but these results were questioned as to their validity.[281,282] In particular, it was shown[281] that the singlet oxygen was actually formed from the reaction of the peroxynitrite with the residual hydrogen peroxide of the peroxynitrite synthesis, rather than directly from the peroxynitrite.

Scheme 34

$$ONOOH \longrightarrow {}^1O_2 + HNO$$

5.4 Diverse Oxidation

The participation of the singlet-oxygen dimol CL in the visible spectral region has been suggested for the reaction of pyrogallol with hydrogen peroxide,[283,284] molecular oxygen,[285,286] and KIO_4 (in the presence of CO_3^{2-})[287] in alkaline solution. Moreover, the singlet-oxygen monomol emission at 1270 nm has been recorded during the peroxyacetyl nitrate decomposition in the presence of NaOH.[288]

The IR−CL of $^1O_2$ at 1270 nm and the emission from triplet benzophenone ($\lambda = 400-500$ nm) have been reported[289,290] for the thermal decomposition of diphenyldiazomethane in the presence of molecular oxygen, which proceeds presumably through a carbonyl-oxide intermediate. Furthermore, the formation of triplet-excited $Ph_2C{=}O$ has been proposed[289] in the reaction of carbonyl oxide with Ph_2CN_2, whereas the singlet oxygen may be formed by the recombination of carbonyl oxides or by energy transfer from triplet-excited benzophenone to triplet molecular oxygen; these chemiluminescent processes are shown in Scheme 35.

Scheme 35

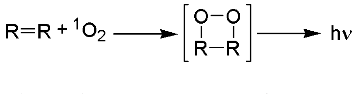
$$Ph_2C^{\cdot}OO^{\cdot} + Ph_2CN_2 \longrightarrow {}^3Ph_2C{=}O^* + Ph_2C{=}O + N_2$$

$$Ph_2C^{\cdot}OO^{\cdot} + Ph_2C^{\cdot}OO^{\cdot} \longrightarrow 2Ph_2C{=}O + {}^1O_2$$

$${}^3Ph_2C{=}O^* + {}^3O_2 \longrightarrow Ph_2C{=}O + {}^1O_2$$

In the case of appropriate olefinic substrates, $^1O_2$ may also mediate[37,291−298] the light emission through the decomposition of intermediary dioxetanes, which are formed through cycloaddition (Scheme 36). For example, dioxetane intermediates have been proposed[291−298] in the chemiluminescent reaction of $^1O_2$ (the $^1O_2$ was generated by the thermal decomposition of endoperoxides and ozonides, by the ClO^-/H_2O_2 system or by photosensitization) with diphenylketene and diphenylketene glycol acetal,[291] *trans*-cyclooctene,[292] alkyl-9,9′-biacridylidenes,[293−295] sulfur-containing seven-membered ring acetylene,[296] and tri- and tetraphenylcyclopropenes.[297] Mechanisms other than the intermediacy of dioxetanes have also been considered[299−301] in singlet-oxygen-mediated CL.

Scheme 36



The photochemiluminescence of air-saturated solutions of sensitizers was attributed to the decomposition of labile peroxides that are formed in the reaction of $^1O_2$ with the pigments.[28,302−308] When $^1O_2$ was generated by a microwave discharge and passed through a solution of chlorophyll *a* in dibutyl phthalate, the singlet-exited dye was produced.[309] In addition, the reaction also generated a very long lasting weak CL, of which the structural identity of the emitter is uncertain.[309]

6. Outlook

Apart from the abundant applications in organic synthesis and the immense environmental and biomedical significance, singlet oxygen has occupied an important place in the world of light-emitting reactions. The monomol and dimol CL of $^1O_2$ has made a sustaining impact on oxidation chemistry and has provided important information on the mechanism of light generation in peroxide reactions. In addition, $^1O_2$ CL has been extensively applied for analytical purposes in chemistry and biochemistry and has become a convenient and powerful tool in the kinetic studies.

Despite the impressive progress attained in the field, a number of important problems merit attention: For instance, one of the enigmas is to understand the behavior and properties of the singlet-oxygen aggregate $(^1O_2)_2$ as a CL emitter in the visible spectral region. This weakly bonded species possesses an extremely short lifetime due to very facile dissociation back into the separate $^1O_2$ molecules, which seriously impedes the quantitative study of this putative intermediate. An intriguing phenomenon concerns the enhancement of the dimol CL by additives such as 1,4-diazobicylco[2,2,2]octane (DABCO). It is uncertain whether this enhancement is due to the influence of DABCO on the nucleation of the incipient oxygen bubbles or whether the radiative properties of the dimol species are favorably altered. Moreover, it is puzzling that the DABCO enhancement effect is not general since it is only observed in $^1O_2$-generating systems such as ClO^-/H_2O_2 and disodium 3,3′-(1,4-naphthylidene)dipropionate endoperoxide.

Potentially worthwhile mechanistic efforts entail the definitive substantiation of the energy transfer from the singlet-oxygen dimol species to a suitable fluorescing acceptor, the so-called singlet-oxygen-dimol-sensitized CL. The elucidation of this phenomenon should provide an understanding of the mechanistic aspects of the light generation in chemical as well as in photochemical systems.

7. Acknowledgments

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