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Review

Photorelease of triplet and singlet oxygen from dioxygen complexes

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ABSTRACT

Photolysis of some dioxygen transition metal complexes leads to the release of oxygen molecules in two electronic states, namely, in the ground triplet state $^3\Sigma_g{}^-$ and the lowest excited singlet state $^1\Delta_g$. The reaction involves electron transfer from the dioxygen moiety to the central metal ion. In the reported cases, the photoreaction of peroxo complexes is activated by ligand-to-metal charge transfer excitation. The mechanism of singlet oxygen photorelease relates to intramolecular energy transfer and differs in principle from the photosensitization process. Consequently, the photorelease can be viewed as a new route to dioxygen activation by spin inversion of the ground state oxygen to singlet oxygen. The quantum yields of singlet oxygen formation are mostly low, nevertheless, they can achieve values as high as 0.5. The data collected so far do not allow specifying general conditions for singlet oxygen release, but they do indicate that the electronic state of released dioxygen is interdependent with the nature of permanent ligands and electronic structure of the excited dioxygen complex.

1. Introduction

The ability of transition metal complexes to bind molecular oxygen has been the subject of numerous studies published since the 1960s, although the first report on binding and releasing an oxygen molecule is ascribed to E. Fremy in 1852. Fundamental research has been summarized in several excellent reviews, to name only a few [1–6]. Current ongoing interest in dioxygen complexes has been motivated by modeling natural respiratory pigments, enzymatic processes catalyzed by oxygenases, and by the development of homogeneous catalysts. More specialized reviews and numerous papers published during the last two decades have been focused on novel dioxygen complexes with various central metals [7–9], homogeneous catalysis [10,11], activation of dioxygen by coordination [12,13], synthetic and modified heme complexes [14,15] and spectroscopic studies [16].

Dioxygen complexes play an important role in the activation of molecular oxygen. The reactions of the oxygen molecule in the ground triplet state, $O_2(^3\Sigma_g{}^-)$, with substrates in the singlet state yielding singlet products are spin forbidden. Circumvention of the spin ban, denoted as activation of dioxygen, can be accomplished in three ways, by (i) coordination of dioxygen, (ii) formation of oxygen radicals, or (iii) spin inversion of $O_2(^3\Sigma_g{}^-)$ to singlet oxygen, usually proceeding as a photosensitized reaction [17–19]. Activation of dioxygen by coordination is a significant issue in homogeneous catalysis as a route to a specific or selective reaction course under mild conditions [11,12].

The photoactivity of dioxygen complexes was described earlier and reviewed by Mäcke and Williams [20]. Relatively few papers have been devoted to an intriguing photoinitiated process by which the bound dioxygen is liberated partly in the excited singlet state $O_2(^1\Delta_g)$. Generation of singlet oxygen in this way differs from photosensitization. The mechanism of photosensitized singlet oxygen formation in which energy is transferred in a bimolecular reaction from the excited triplet states of sensitizer molecules to the ground state oxygen $O_2(^3\Sigma_g{}^-)$ is discussed in more detail in [21–24].

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Formation of $O_2(^1\Delta_g)$ by photorelease from a dioxygen complex proceeds by a fundamentally different monomolecular mechanism [25] that so far has not been fully understood. A similar process, liberation of dioxygen in both electronic states, appears in organic endoperoxides on irradiation or thermal treatment [26]. In spite of the structural difference, comparison of photochemical behavior of both types of compounds could be of interest.

Generally speaking, the resulting electronic state of the liberated dioxygen can be affected by excitation wavelength, photophysical properties of the dioxygen complex, dioxygen–central ion bond, nature of the other ligands, and the microenvironment. In the context of this paper, dioxygen excited to the lowest singlet state $^1\Delta_g$ is referred to as "singlet oxygen," or $^1O_2$.

The photorelease phenomenon provides a new insight into dioxygen photochemistry. Even small but conveniently localized quantities of photoreleased $^1O_2$ may be significant in specific oxidations or diagnostics. Laser-flash induced photorelease of dioxygen and its fast-trapping by hemes, cytochromes, or their models generates information on their functioning [27,28], but in this context the formation of $^1O_2$ has not yet been examined. Even a small fraction of $^1O_2$ in the photoreleased dioxygen might represent a danger for biological oxygen-dependent reactions [29]. In a broader context, photorelease can become an experimental route of directed liberation of small molecules coordinated in metal complexes [30,31].

This paper reviews advances in dioxygen metal complexes sharing the noteworthy feature of dioxygen release controlled by light. Basic structural and kinetic properties of dioxygen complexes related to the focus of this review are presented. We describe the photorelease of dioxygen from the point of view of potential applications (e.g., fast *in situ* dioxygen delivery). Particular attention is paid to the appealing effect that the dioxygen can be photochemically liberated in two electronic states and complexes with the proven formation of $^1O_2$ are mutually compared. This arrangement allows the selection of dioxygen complexes for applications where the electronic state of liberated dioxygen might be a limiting parameter. The fundamental properties of published photoactive complexes are reviewed in Table 1 .

2. Dioxygen complexes

Although dioxygen complexes of diverse transition metals differ in particulars, some common features exist that should be briefly discussed. Dioxygen can be bound either to one central ion or to bridge two metal ions. The binding is coupled with a shift of electron density from the central ion to the antibonding $2p\pi^*$ orbitals of the dioxygen moiety and, consequently, the bound dioxygen approaches the oxidation state of superoxide $O_2{}^-$ or peroxide $O_2{}^{2-}$ anions. The main structural motifs of superoxo and peroxo moieties of the η^1-superoxo, μ-superoxo, η^2-peroxo, and μ-peroxo structures are depicted in Fig. 1.

Binding of dioxygen and the shift of the electron density within the complex necessarily affect the length of the O–O bond and possibly also the process of photoelimination of dioxygen. For example, in cobalt complexes the O–O distances in the μ-superoxo motif vary in the range of 1.243–1.353 Å and in the μ-peroxo motif, they vary between 1.308 and 1.488 Å [6]. Stretching frequencies ν_{O-O} of superoxo complexes fall within 1030–1195 cm^{-1}, while peroxo complexes display frequencies in the range of 750–950 cm^{-1}. The lower frequencies reflect the more distinct shift of electrons towards the dioxygen moiety [6,10].

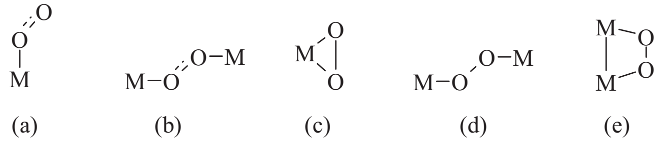


Fig. 1. Dioxygen binding motifs: (a) η^1-superoxo, (b) μ-superoxo, (c) η^2-peroxo, (d) μ-peroxo and (e) trapezoid-peroxo structures.

In the binuclear iridium complex $[I_2(CO)_2Ir_2(O_2)(Ph_2PCH_2PPh_2)_2]$ (PPh_2 – diphenylphosphine) the peroxo moiety bridges two iridium atoms linked by a metal–metal bond whereof ensues an unaccustomed trapezoid arrangement (Fig. 1) [32,33]. The O–O distance of 1.58 Å is unusually long and with respect to the Ir–Ir distance of 2.705 Å, points to a strain imposed by the metal–metal bond. The binding of dioxygen is irreversible. A similar binding motif was established in a dimetallaborane in which two platinum atoms occupy two neighboring sites of a twelve-vertex boron cluster (Fig. 2) with the Pt–Pt distance of 2.7143 Å [34,35]. In this case, however, dioxygen is bound reversibly. The O–O distance of 1.434 Å is typical for the μ-peroxo structure. Photochemistry of the trapezoid platinum complex will be discussed in Section 2.2.

The generally accepted reaction mechanism of a dioxygen complex formation first proposed by Wilkins has been based on stopped-flow studies of cobalt complexes [36]. The two-step mechanism comprises the formation of four basic types of complexes (Eqs. (1) and (2)).

$$\mathrm{CoL} + \mathrm{O_2} \rightleftarrows \mathrm{O_2CoL}, \quad k_1, k_{-1} \tag{1}$$

$$\mathrm{O_2CoL} + \mathrm{CoL} \rightleftarrows \mathrm{LCoO_2CoL}, \quad k_2, k_{-2} \tag{2}$$

The first step (Eq. (1)) holds for the production of η^1-superoxo and η^2-peroxo complexes [36,37]. The η^1-superoxo complexes are either final products, usually in aprotic solvents, or are intermediates in the generation of the μ-peroxo species (Eq. (2)). The direct route to cobalt μ-superoxo complexes starts by *in situ* photoreduction of a Co(III) complex in dioxygen saturated solution, followed by reactions (1) and (2) [38,39]. Nevertheless, the standard preparation of μ-superoxo complexes is the one-electron oxidation of a μ-peroxo species [5]. The rate constants k_1 for most complexes are in the range of 10^3–10^5 M^{-1} s^{-1}; for hemes the constants can exceed 1×10^7 M^{-1} s^{-1} [36,40,41]. This difference may be significant in rebinding of photoreleased dioxygen in biological systems.

2.1. Photorelease of dioxygen from dioxygen complexes

The term photorelease denotes photoinitiated liberation of molecular oxygen from dioxygen complexes with the stipulation

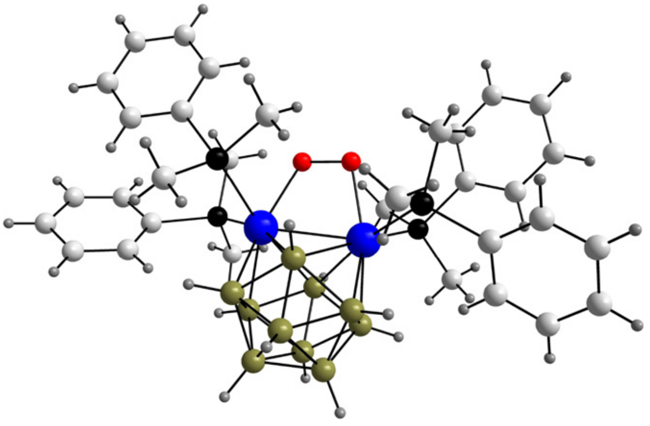


Fig. 2. Representation of the crystallographically obtained molecular structure of the trapezoid-peroxo complex $[(PMe_2Ph)_4Pt_2(O_2)(B_{10}H_{10})]$ (red, oxygen; blue, platinum; green, boron; black, phosphorus atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 1
Photorelease of dioxygen from dioxygen complexes.

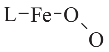
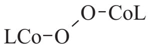
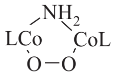
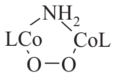
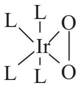
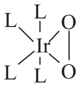
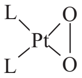
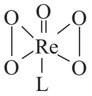
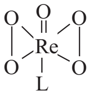
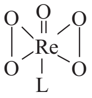
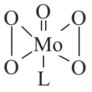
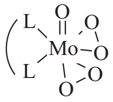
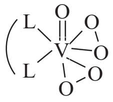
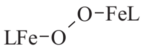
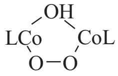
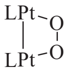
Motif	$^1O_2$	$^3O_2$	Solvent	Ref.	Note
	?	+	Tetrahydro-furan	[28]	η^1-superoxo $\Phi^{532}_{O_2} = 0.18–0.60$ 198 K
	0	+	H_2O	[44]	μ-superoxo $\Phi^{320}_{O_2} = 0.30$ $\Phi^{350}_{O_2} = 0.24$
	0	+	H_2O	[44]	Dibridged μ-superoxo $\Phi^{320}_{O_2} = 0.49$ $\Phi^{350}_{O_2} = 0.40$
	?	+	H_2O	[45]	Dibridged μ-superoxo $\Phi^{320}_{O_2} = 0.065$ $\Phi^{350}_{O_2} = 0.005$
	0	+	Benzene Ethanol Acetonitrile	[47]	η^2-peroxo
	+	+	CH_2Cl_2 Benzene	[25]	η^2-peroxo $\Phi^{308}_{\Delta} = 0.03$ $\Phi^{308}_{P} = 0.43$
	+	+	$CHCl_3$	[54]	η^2-peroxo
	0	+	CH_2Cl_2	[48]	Oxo-η^2-diperoxo
	?	+	Acetonitrile	[49]	Oxo-η^2-diperoxo O–O splitting
	?	+	Ether/H_2O	[50]	Oxo-η^2-diperoxo, dismutation of peroxo groups
	+	0	Acetonitrile	[55]	Oxo-η^2-diperoxo $\Phi^{266}_{\Delta} = 0.42$
	+	+	CH_2Cl_2	[56]	Oxo-η^2-diperoxo $\Phi^{308}_{\Delta} = 0.13–0.19$ $\Phi^{308}_{P} = 0.17–0.46$
	+	+	H_2O, D_2O	[59,60]	Oxo-η^2-diperoxo $\Phi^{362}_{\Delta} = 0.001–0.007$
	+	+	Ethanol-H_2O	[58]	μ-peroxo $\Phi^{333}_{O_2} = 5 \times 10^{-4}$
	?	+	H_2O	[27,46,52]	Dibridged μ-peroxo $\Phi^{355}_{O_2} = 0.04$ [27] $\Phi^{314}_{O_2} = 0.5$ [52] $\Phi^{366}_{O_2} = 0.0047$ [46]

Table 1 (*Continued*)

Motif	$^1O_2$	$^3O_2$	Solvent	Ref.	Note
	+	+	CH_2Cl_2	[61]	Trapezoid-peroxo $\Phi_{O_2}^{308} = 0.58$ $\Phi_{\Delta}^{308} < 0.01$

?, $^1O_2$ not examined; 0, $^1O_2$ not found; +, $^1O_2$ detected; L, ligand; Φ_P, photolysis quantum yield; Φ_{O_2}, quantum yield of the dioxygen release; Φ_Δ, quantum yield of the singlet oxygen formation. The superscripts of respective quantum yields represent the wavelength used for excitation.

that the cleavage of the O–O bond is not involved. Evidently, in the process one or two electrons are transferred from the dioxygen moiety to the metal center. One of the first reports showed that exposure of the μ-superoxo complex $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ to sunlight yielded dioxygen and Co^{2+} [42]. Experiments with the μ-superoxo group labeled by $^{18}O_2$ proved that dioxygen evolved on photodecomposition had the same isotopic composition as the irradiated complex [43]. It can be concluded from this result that one electron is transferred from the $O_2{}^-$ moiety to Co(III) without splitting the O–O bond.

From the photochemical point of view it is possible that the oxygen molecule released from the excited complex is in the excited singlet state. The first study intentionally exploring the release of $^1O_2$ from two μ-superoxo cobalt complexes was published in 1971 [44]. With continuous irradiation at wavelengths of 300–400 nm, μ-superoxo and μ-amido-μ-superoxo complexes decomposed and the amount of evolved dioxygen corresponded to the stoichiometry of the following equations:

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{5+} + H_2O + 5H^+ \xrightarrow{h\nu} [Co(NH_3)_5(H_2O)]^{3+} + Co^{2+} + O_2 + 5NH_4^+ \quad (3)$$

$$[(NH_3)_4Co(O_2, NH_2)Co(NH_3)_4]^{4+} + H_2O + 5H^+ \xrightarrow{h\nu} [Co(NH_3)_5(H_2O)]^{3+} + Co^{2+} + O_2 + 4NH_4^+ \quad (4)$$

The quantum yields of the dioxygen release, Φ_{O_2}, upon 320 and 350 nm irradiation, were 0.30 and 0.24 in the reaction (3), respectively; in the reaction (4), the Φ_{O_2} values were 0.49 and 0.40 at the same wavelengths. The absorption bands near 320 nm were assigned to superoxide-to-cobalt charge transfer transitions. This indicates that the dioxygen release proceeds through charge transfer from the dioxygen moiety to the metal center. The presence of $^1O_2$ in the evolved oxygen was probed by 1,3-cyclohexadiene with negative results. Quite analogous photochemical behavior and reaction stoichiometry displayed the dibridged μ-superoxo complex with ethylenediamine ligands $[(en)_2Co(O_2,NH_2)Co(en)_2]^{4+}$ (en – ethylenediamine) [45]. The quantum yields Φ_{O_2} on 320 and 350 nm irradiation were substantially lower than in the previous cases and amounted to 0.065 and 0.005, respectively. The difference is probably due to the donor properties of the ligand and, consequently, to the higher charge density on the bridging superoxide moiety. The presence of $^1O_2$ was not examined. In view of the latter studies, the observations reported in [43,44] are essential for investigation and interpretation of the photochemical mechanism of the $^1O_2$ release.

A dibridged μ-peroxo complex $[(en)_2Co(O_2,OH)Co(en)_2]^{3+}$ in aqueous basic solution (pH 8.1–10.4) continuously irradiated at 366 nm released reversibly dioxygen according to Eq. (5) [46].

$$[(en)_2Co(O_2, OH)Co(en)_2]^{3+} \xrightarrow{h\nu} 2[Co(en)_2(H_2O)_2]^{2+} + O_2 \quad (5)$$

The reaction (5) is followed by a slower irreversible decomposition of the cobalt complex. The maximal quantum yield Φ_{O_2} was 0.0047 at pH 9.0 at 25 °C. The formation of $^1O_2$ was not considered. A similar dibridged μ-peroxo complex $[(en)_2Co(O_2,NH_2)Co(en)_2]^{3+}$ is much less reactive photochemically and no deoxygenation reaction was observed [46].

Additional information on the dioxygen release was obtained through studies of several η^2-peroxo complexes [47–49]. Of the three iridium η^2-peroxo complexes $[((PPh_2)_2ethane)_2IrO_2]^+$, $[((PPh_2)_2ethylene)_2IrO_2]^+$ and $[Cl(CO)(PPh_3)_2IrO_2]$ (PPh_2 – diphenylphosphine, PPh_3 – triphenylphosphine), only the last one loses dioxygen when a benzene solution is purged with inert gas and therefore solutions were irradiated in air or saturated with oxygen [47]. Ethanol solutions of the two other complexes were irradiated under an inert atmosphere. All three complexes liberated dioxygen when continuously irradiated at 366 nm and the reaction could be reversed by introducing dioxygen in the dark. The quenching reaction with tetramethylethylene did not prove the formation of $^1O_2$. In the light of more recent investigation, this result will be the subject of further discussion in Section 2.2.

Photochemical reactions of methylrhenium oxo-η^2-diperoxo complex $[CH_3Re(O_2)_2O]$ were investigated in the context of homogeneously catalyzed oxygenation reactions [48]. The complex released dioxygen when continuously irradiated at 312 nm in methylene chloride. Absorption spectra of the irradiated complex document photoelimination of both peroxo groups and formation of the methylrhenium oxo complex as the only photoproduct. Since the quantum yield of the singlet oxygen formation, Φ_Δ, determined by phosphorescence at 1274 nm, was lower than 1×10^{-3}, the authors did not consider it positive proof of the presence of $^1O_2$. The low quantum yield may be due to quenching of $^1O_2$ by the parent methylrhenium oxo-η^2-diperoxo complex of which the quenching rate constant was determined to be $1.4 \times 10^7\ M^{-1}\ s^{-1}$. Wang and Espenson confirmed photoelimination of dioxygen from the same complex in acetonitrile irradiated by $\lambda > 400$ nm [49]. In this case, however, the authors infer that the mechanism of dioxygen liberation involves splitting the O–O bond of the peroxo group. The electronic state of dioxygen was not determined. A more recent study on $[CH_3Re(O_2)_2O]$ in water saturated ether reported dioxygen release upon irradiation at 254 nm [50]. In early stages, the reaction could be reversed by adding hydrogen peroxide. The absorption spectra suggest that the reaction proceeds according to the following equation:

$$CH_3Re(O_2)_2O \rightarrow CH_3Re^{VII}O_3 + O_2 \quad (6)$$

with the methyl Re^{VII} monoperoxo complex as a primary product. The formation of $^1O_2$ was not considered. Taking into consideration that the irradiation wavelength 254 nm corresponds to intraligand charge transfer (ILCT) excitation of the peroxo groups of which only one oxygen molecule is released, the following reaction mechanism seems plausible: In the rearrangement which succeeds the excitation, the electron density shifts from one peroxo group to the other so that the peroxo groups cease to be equivalent. The asymmetric charge distribution invokes peroxide dismutation to O_2 and $2O^{2-}$ and formation of an oxidic product [50]. This mechanism of dioxygen liberation differs from that discussed in [44], in which electron transfer proceeds from the dioxygen moiety to the metal center without splitting the O–O bond.

From the results presented above, it can be concluded that photoinitiated dioxygen release occurs when the process is initiated by ligand-to-metal charge transfer (LMCT) excitation of the bound peroxo group (300–400 nm) followed by electron transfer to the central metal and dioxygen liberation. Provided that for the detection of $^1O_2$ less specific indirect chemical methods were in some cases employed, negative results may not be conclusive. Excitation at wavelengths less than 300 nm corresponding to excitation of the peroxo group (ILCT) evokes dismutation. Excitation corresponding to metal-to-ligand charge transfer (MLCT) induces electron transfer to the dioxygen moiety and liberation of hydrogen peroxide and eventually dismutation to water and dioxygen [51]. The mechanisms involving dismutation of hydrogen peroxide does not lead to the release of singlet oxygen.

A deeper insight into the mechanism of dioxygen photorelease was provided by studies employing laser flash excitation in the nanosecond time scale, though without seeking to explore the spin state of photoreleased dioxygen.

A study of the kinetics of dioxygen photoelimination from μ-peroxo complexes was motivated by a need for fast *in situ* production of dioxygen in the presence of biomolecules binding dioxygen and directing oxygen redox reactions, as are heme proteins and cytochromes. Photoelimination of dioxygen from dibridged μ-peroxo $[(bipy)_2Co(O_2,OH)Co(bipy)_2]^{3+}$ perchlorate (bipy – 2,2′-bipyridine) excited at 355 nm appeared at 40 ns or on a faster time scale [27]. The photoreaction proceeded in an aqueous solution at physiological pH 7.4 under nitrogen. The quantum yield Φ_{O_2} of 0.04 is significantly lower than are the yields reported for the cobalt μ-superoxo complexes [44,45]. This study produced original information on the kinetics of dioxygen release. A similar approach was followed up in further investigations using the same dibridged μ-peroxo complex as in [27]. Ludovici et al. [52] prepared nitrate salt of the complex and reported the value of Φ_{O_2} as high as 0.5 on 314 nm irradiation. The substantial difference from the value cited above was explained by better solubility of nitrate salt. Thermodynamic parameters of dioxygen photorelease from $[(bipy)_2Co(O_2,OH)Co(bipy)_2]^{3+}$ and its analog with 1-phenanthroline ligands were obtained by means of photoacoustic calorimetry [53]. The enthalpy and volume changes were measured at the excitation wavelength of 355 nm. The results confirm the splitting of four Co(III) bonds, reduction of Co(III) to Co(II), and the time scale of the photochemical process below 50 ns.

Kinetic data on dioxygen photoelimination from η^1-type superoxo complexes of synthetic hemes were obtained in low temperature experiments in tetrahydrofuran [28]. These complexes were prepared by low temperature oxygenation of synthetic hemes. Excitation by 355 and 532 nm pulses at 198 K resulted in the immediate release of dioxygen. The quantum yields Φ_{O_2} vary from the remarkably high value of 0.60 to 0.18 and are close to that of oxy-myoglobin. The rate constants of dioxygen rebinding, k_1, to the deoxygenated complex are of the order of $10^5\ M^{-1}\ s^{-1}$ at 198 K. As a matter of fact, the dioxygen rebinding reaction closes the cyclic process of excitation, O_2 photorelease and re-formation of the parent dioxygen complex. In this context, the relatively high values of Φ_{O_2} and k_1 may be significant if $^1O_2$ would be produced.

2.2. Photorelease of singlet oxygen from dioxygen complexes

Detection of $^1O_2$ was positive in the platinum η^2-type peroxo complex $[(PPh_3)_2PtO_2]$ [54]. Dioxygen was released when the complex dissolved in $CHCl_3$ was continuously irradiated at 310 nm. After irradiation, the parent peroxo complex was regenerated by saturation of the solution with oxygen. Singlet oxygen was detected by ESR spectroscopy using 2,2,6,6-tetramethylpiperidine as a singlet oxygen scavenger. From calculations of the lowest energy transition, it follows that the irradiation wavelength corresponds to dioxygen intraligand transition with a LMCT contribution.

Table 2
Quantum yields of photolysis, Φ_P, and singlet oxygen formation, Φ_Δ, by the oxo-η^2-diperoxo complex $[(HMPA)MoO(O_2)_2]$ (HMPA – hexamethylphosphoric triamide) in degassed acetonitrile at different excitation wavelengths [55].

λ_{ex} (nm)	Φ_P	Φ_Δ
366	0.06	–
337	0.10	0.09 ± 0.03
308	0.25	0.25 ± 0.03
266	0.45	0.42 ± 0.05
254	0.40	–

The oxo-η^2-diperoxo molybdenum complex $[(HMPA)MoO(O_2)_2]$ (HMPA – hexamethylphosphoric triamide) was continuously irradiated at several wavelengths in the range of 254–366 nm or excited by laser pulses of 266, 308 and 337 nm [55]. In the course of the irradiation at 313 nm, one of the peroxo groups remained bound in the photoproduct and only one oxygen molecule per molecule of the parent complex was photoreleased. The release of $^1O_2$ was proven by a time-resolved measurement of the $^1O_2$ phosphorescence at 1276 nm. The quantum yields of photolysis of the complex, Φ_P, and Φ_Δ are summarized in Table 2. From the same course of the wavelength dependence of both the quantum yields, it follows that the photoreleased dioxygen is quantitatively generated in the singlet state. The explanation of this result stems from the fact that photorelease of $^1O_2$ from an upper excited singlet state of a LMCT character occurs with 100 percent effectiveness. It appears that no intersystem crossing competes with the formation of $^1O_2$ that proceeds as an adiabatic process. This is the first, and hitherto only, observation of the photorelease of dioxygen exclusively in the singlet state.

Extensive study was devoted to similar molybdenum oxo-η^2-diperoxo complexes modified with N,N′ chelating ligands pyrazolylpyridine and imidazolylpyridine [56]. Both complexes existing in two isomeric forms liberated dioxygen when continuously irradiated. Time-resolved phosphorescence measurements proved the formation of $^1O_2$, however, a comparison of Φ_Δ with Φ_P showed that only a fraction of the eliminated dioxygen was in the singlet state. In contrast to the complex $[(HMPA)MoO(O_2)_2]$ [55] described above, the photorelease of both $^1O_2$ and $^3O_2$ indicates an increased participation of intersystem crossing. Presumably, the reason for the competitive intersystem crossing is the proximity of the excited states evoked by the chelating ligands.

Iridium η^2-peroxo complexes $[Cl(CO)(PPh_3)_2IrO_2]$ and related Vaska's compounds have been known to release oxygen when irradiated [47]. More recent laser flash photolysis of this complex and of its Br and I analogs in degassed methylene chloride at 308 nm indicated the formation of $^1O_2$ [25]. The decrease of the signal with each laser shot corroborates the formation of $^1O_2$ by photorelease and not by photosensitization. Because the parent iridium complexes quench $^1O_2$ with a high quenching rate constant of the order of $10^8\ M^{-1}\ s^{-1}$, the quantum yield Φ_Δ could have been determined only in respect to $[Cl(CO)(PPh_3)_2IrO_2]$ and amounts to 0.03 ± 0.01. Fast quenching of $^1O_2$ and low quantum yields were evidently why singlet oxygen was not detected in the earlier paper [47]. In contrast with the oxodiperoxo complex $[(HMPA)MoO(O_2)_2]$ photoreleasing exclusively $^1O_2$ [55], the iridium complexes produce both singlet and triplet oxygen (ratio $^1O_2/^3O_2 = 0.08$). Photorelease of ground state oxygen indicates that intersystem crossing from the upper excited singlet state of the complex competes with the adiabatic process generating $^1O_2$ [25]. The competitive intersystem crossing is facilitated by the proximity of the excited states and manifests itself by the formation of ground state oxygen.

The μ-peroxo complex $[(TSPC)Fe(O_2)Fe(TSPC)]$ (TSPC - 4,4′,4″,4‴-tetrasulfophthalocyanine) is stable in an air saturated aqueous solution for about 1 h. In a subsequent slow reaction it undergoes irreversible oxidation into a μ-oxo complex [57].

Table 3
Quantum yields of the singlet oxygen formation, Φ_Δ, at 362 nm irradiation and quenching rate constants of $^1O_2$, k_q, by some oxo-η^2-diperoxo VO complexes [60].

Complex[a]	Φ_Δ^{362}	k_q ($M^{-1}\,s^{-1}$)
$Na[VO(O_2)_2(phen)]$	0.007	1.3×10^7
$Na[VO(O_2)_2(4\text{-Mephen})]$	0.0058	4.4×10^7
$Na[VO(O_2)_2(5,6\text{-}Me_2phen)]$	0.005	6.4×10^7
$Na[VO(O_2)_2(4,7\text{-}Me_2phen)]$	0.005	3.5×10^7
$NH_4[VO(O_2)_2(5\text{-}NO_2phen)]$	0.0047	8.4×10^7
$Na[VO(O_2)_2(3,4,7,8\text{-}Me_4phen)]$	0.0027	7.1×10^7
$Na[VO(O_2)_2(bipy)]$	0.0056	0.8×10^7
$Na[VO(O_2)_2(4,4'\text{-}Me_2bipy)]$	0.0026	0.8×10^7

[a] phen, 1,10-phenanthroline; bipy, 2,2′-bipyridine; Me, methyl.

A photoinitiated reaction induced by irradiation at 333 nm in water/ethanol solution under argon proceeds according to the equation

$$[(TSPC)Fe(O_2)Fe(TSPC)] \xrightarrow{h\nu} 2Fe^{II}TSPC + O_2 \qquad (7)$$

with a quantum yield Φ_{O_2} of 5×10^{-4} [58]. The formation of $^1O_2$ was proven indirectly by quenching reactions with diphenylacetylene. Photorelease is most probably due to a LMCT ($O_2 \rightarrow Fe^{III}$) transition induced by the preceding intraligand excitation of the dioxygen moiety.

Two studies exploring $^1O_2$ release from oxo-η^2-diperoxo VO complexes were motivated by the observation that these complexes possess a DNA photocleavage activity [59,60]. The active agents of the oxidative DNA cleavage can be hydroxyl radicals and/or $^1O_2$. The photolysis at 362 nm of $[VO(O_2)_2L]$ (L are 2,2′-bipyridine or 1,10-phenanthroline ligands) in D_2O produces $^1O_2$ with quantum yields Φ_Δ of the order of 10^{-3} (Table 3). The low values of Φ_Δ can be ascribed to quenching of $^1O_2$ by the peroxo complexes as follows from the high values of the quenching rate constants also listed in Table 3. In spite of the low Φ_Δ the advantage of diperoxo VO complexes consists in recognizing and site-specific binding to DNA.

Of the two known trapezoid dioxygen complexes only the icosahedral bimetallaborane cluster $[(PMe_2Ph)_4Pt_2(B_{10}H_{10})]$ (PMe_2Ph – dimethylphenyl phosphine) binds dioxygen reversibly to provide the complex $[(PMe_2Ph)_4Pt_2(O_2)(B_{10}H_{10})]$ (Fig. 2) [34,35]. It is the first reported dioxygen complex with an electron-deficient boron cluster as a ligand. Localization of the dioxygen moiety across the diplatinum unit evokes a significant distortion of the coordination geometry of the Pt–Pt unit. The oxygenation–deoxygenation processes can be repeated by intermittent irradiation, i.e., during an irradiation period (>370 nm) dioxygen is photoreleased and during a "dark" period dioxygen rebinds to the deoxygenated complex [61]. Transient absorption spectroscopy in CH_2Cl_2 disclosed that dioxygen is released with the quantum yield Φ_{O_2} as high as 0.58 ± 0.03 (308 nm) in the picosecond timescale. The formation of $^1O_2$ was proven by its phosphorescence. The low value of the $^1O_2$ quantum yield, $\Phi_\Delta < 0.01$ (308 nm), indicates that participation of the reaction leading to the excited product $^1O_2$ is limited by the competing intersystem crossing. Because the transient absorption spectroscopy of the parent complex did not detect any excited transients able to interact with dioxygen, the photosensitized formation of $^1O_2$ was excluded. To the best of our knowledge, $[(PMe_2Ph)_4Pt_2(O_2)(B_{10}H_{10})]$ is the only example where a complex photoreleases dioxygen bound across a metal–metal bond.

Results published to date on photorelease of dioxygen in singlet and triplet states are reviewed in Table 1. Dioxygen photorelease has been documented for all dioxygen-metal binding motifs. Since some papers did not pursue the spin state of the released dioxygen, formation of at least small quantities of $^1O_2$ cannot be excluded. However, formation of $^1O_2$ was proven in several cases, most of which were the η^2-peroxo type, one a μ-peroxo type complex, the other a trapezoid peroxo-type complex.

2.3. Mechanism of dioxygen photorelease

The most frequent route to $^1O_2$ production is photosensitization by organic dyes or complexes of non-transition metals *via* excitation of the sensitizer to the triplet state and subsequent intermolecular energy transfer to an oxygen molecule. Depending on their electronic structure, some complexes of transition metals are also efficient sensitizers [21]. Electronic spectra of these complexes exhibit transitions assigned as inner sphere metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), and various ligand centered transitions [62,63].

Most studies on charge transfer excited states have focused on complexes with luminescent MLCT states. Certain diimine ruthenium(II), platinum(II) and palladium(II) complexes have relatively long-living triplet MLCT states. Their quenching by dioxygen produces $^1O_2$ with quantum yields dependent on the nature of ligands [21]. Similarly, the photosensitizing activity of iridium (III) and rhenium (I) complexes is based on triplet MLCT states [64].

It is obvious that the mechanism described above cannot explain photorelease of $^1O_2$ from dioxygen complexes. Photorelease is started by LMCT excitation of a dioxygen complex and proceeds as an intramolecular energy transfer. As already noted, photorelease of $^1O_2$ was proven for transition metal - dioxygen complexes of the peroxo type. With respect to peroxo complexes, it was suggested that the photoactivity of the excited states was due to the redox properties of the peroxide ligand [51]. It follows from the fact that the $O_2{}^{2-}$ ligand can act as a charge transfer donor or acceptor and hence the oxidation of the peroxo ligand to dioxygen (i.e., the release of an oxygen molecule) should be induced by LMCT excitation. Reduction of the peroxo ligand should be initiated by MLCT excitation. This premise is consistent with the observation that the photolysis of Cr(IV) diperoxide excited in the MLCT band proceeds as a two-electron transfer from the metal to the peroxo ligands and no dioxygen is released [51]. This mechanism is completely different from that of sensitization on the MLCT excitation described above. The principal difference consists in the redox properties of the $O_2{}^{2-}$ ligand.

Due to the reducing character of O_2^{2-}, many peroxo complexes of Co(III), Fe(III), V(V), etc. have LMCT transitions [62,63] leading to the release of dioxygen in the ground state and/or in the excited singlet state [51] (Table 1). It should, nevertheless, be borne in mind that the degree of peroxide and metal orbital mixing affects the energy required for LMCT. Any changes in the metal coordination sphere can therefore induce changes in the photorelease of dioxygen.

Organic endoperoxides are capable of releasing dioxygen as $^3O_2$ or $^1O_2$ upon thermal treatment or excitation into upper excited states S_n with $n \geq 2$ [26,65,66]. Nevertheless, the photochemical behavior is not fully analogous with the photolysis of dioxygen complexes. In endoperoxides the peroxo group is covalently bound to two carbons, whereas in dioxygen complexes the dioxygen moiety is coordinated to the central metal ion or ions, with a partial charge transfer to dioxygen. Endoperoxides are formed by a direct [4 + 2] cycloaddition of $^1O_2$ to aromatic compounds. The photoinitiated ($\lambda > 250$ nm) reverse reaction starting with the C–O bond cleavage – cycloreversion – yields both singlet and triplet oxygen. The yields of $^1O_2$ can be high, e.g., in dibenzoperylene-8,16-dione endoperoxide the yield reaches 100 percent [65]. According to theoretical predictions, singlet oxygen may be primarily generated as $O_2(^1\Sigma_g{}^+)$ that by a rapid internal conversion yields the determined $O_2(^1\Delta_g)$ [65,67].

The metal complexes, on the other hand, react with ground triplet oxygen and form superoxo or peroxo complexes of various structural motifs. Moreover, the η^2-peroxo complexes, some

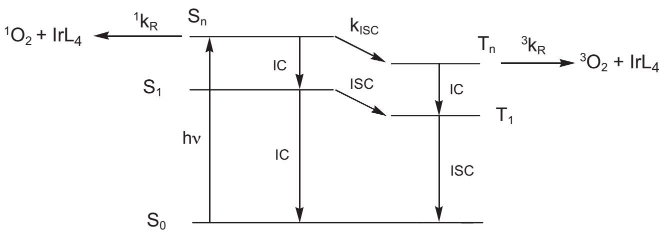


Fig. 3. Energy diagram for the photorelease of dioxygen from the η^2-peroxo complex $IrL_4(O_2)$ according to [25]. (IC, internal conversion; ISC, intersystem crossing.)

of which release $^1O_2$, have no analogy among endoperoxides. The similarity of both processes leading to $^1O_2$, cycloreversion and photorelease, rests in the adiabatic transition from an upper excited singlet state. A plausible explanation of the photoreaction yielding $^1O_2$ has been based on the behavior of oxodiperoxo Mo complexes, one of which releases $^1O_2$ exclusively [55,56]. Singlet oxygen is generated by an allowed transition from an upper singlet state, whereas the competitive intersystem crossing to a photochemically active triplet state yields oxygen in the ground triplet state. These transitions are according to Seip and Brauer [25] schematically presented in Fig. 3 where ^ik_R (i = 1, 3) defines the rate of $^1O_2$ or $O_2(^3\Sigma_g^-)$ release. The overall quantum yield of the dioxygen release Φ_{O_2} is given as $\Phi_{O_2} = \Phi_\Delta + \Phi(O_2(^3\Sigma_g^-))\Phi_{ISC}$. The extent, to which the particular competitive process participates, apparently depends on the difference between the excited states and hence also on the nature of ligands. A high intersystem crossing rate k_{ISC}, effectively competing with ^1k_R leading to $^1O_2$, can be expected due to the high spin-orbit coupling caused by the central metal. A more detailed description, however, requires quantum chemistry calculations.

3. Conclusions and prospects

The results introduced in this review disclose that the general prerequisite for photorelease of dioxygen without breaking the O–O bond is excitation in the LMCT bands in the UV region ($\lambda_{excit} < 400$ nm) [51]. Wavelengths substantially shorter than 300 nm can split the O–O bond. At this point it should be recalled that photorelease of O_2 irrespective of its electronic state has been observed for all types of dioxygen complexes. Fundamental observations on $^1O_2$ release were accomplished with a limited number of peroxo-type complexes of a few transition metals. The release of $^1O_2$ from superoxo complexes was probed in only two cases and that with negative results obtained by indirect methods [44]. Hence, any conclusions concerning the correlation between the type of dioxygen complexes and photorelease of $^1O_2$ can hardly be put forward.

Interest in this area has been driven mainly by the development of useful compounds for studying processes initiated by dioxygen. Dioxygen complexes that can instantaneously release spatially and/or temporally well-defined fluxes of oxygen under an external trigger are necessary especially for kinetic studies of complex biological systems. One application concerns the mechanistic investigation of oxygen-dependent enzymes such as cytochrome oxidases [27,52], oxidation of reduced flavin mononucleotide [68], or the migratory response of bacteria [69]. For these experiments the complex $[(bipy)_2Co(O_2,OH)Co(bipy)_2]^{3+}$ was used; this photoreleases oxygen even at 100 K [68]. This characteristic promises utilization of the complex under conditions in which unstable intermediate states of oxygen-dependent enzymes have prolonged lifetimes. Another prospect for the future, though at present it might be viewed as a minor one, is in the development of compounds producing $^1O_2$. The method offers fast and a precisely localized amount of $^1O_2$ molecules, e.g., for specific use in DNA splitting [59,60,70]. On the other hand, formation of $^1O_2$ can be a drawback during the studies of oxygen dependent enzymes, respiratory pigments and their models [27,28,31] because even small quantities of $^1O_2$ may be harmful to biological systems [29]. Photorelease of $^1O_2$ should be regarded as a new mechanism of dioxygen activation by spin inversion different from the more frequent sensitization. The release of $^1O_2$ should be considered in all photoinitiated reactions in which dioxygen is liberated from a dioxygen complex.

Furthermore, the detailed photophysical mechanism of the $^1O_2$ release from dioxygen complexes is interesting *per se*. To arrive at a comprehensive understanding of the phenomenon, further experiments will necessitate systematic selection of representative dioxygen complexes of various types (e.g., central ion, ligands, dioxygen bond) together with quantum chemical calculations establishing the character and order of the electronic states of the complexes.

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