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Review

Photochemistry of peroxo complexes induced by LMCT, MLCT and peroxide IL/LLCT excitation

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Contents

Abstract

Peroxide is a reductant as well as an oxidant. It follows that O_2^{2-} as a ligand can serve as CT donor, but also as CT acceptor. In combination with oxidizing and reducing metals low-energy ligand-to-metal (LMCT) and metal-to-ligand (MLCT) transitions, respectively, occur. Photoredox reactions originating from such LMCT and MLCT excited states are well known. In the case of diperoxo complexes $M(O_2)_2$, peroxide intraligand transitions play an important role. IL excitation is followed by interligand charge transfer (LLCT) within the $(O_2^{2-})_2$ moiety. As a result, a photodismutation to $2O^{2-}$ and O_2 takes place. Accordingly, IL excitation of $MeRe^{VII}(O_2)_2O$ leads to the formation of $MeRe^{VII}O_3$ and O_2.

Keywords: Electronic spectra; Photochemistry; Charge transfer; Peroxo complexes

1. Introduction

A variety of peroxo complexes has been shown to be light sensitive [1–6]. The photoreactivity is apparently associated with the peroxo ligand, which can undergo redox transformations. The nature of the reactive excited states might thus be related to the redox properties of O_2^{2-}. Peroxide is not only an oxidant but also a reductant. As a further consequence, it can undergo a dismutation. In aqueous solution peroxide exists as H_2O_2, but the redox potentials are, of course, pH dependent.

$$H_2O_2 + 2H^+ + 2e^- \leftrightarrows 2H_2O \quad E^0 = 1.77\,V \tag{1}$$

$$H_2O_2 \leftrightarrows O_2 + 2H^+ + 2e^- \quad E^0 = 0.68\,V \tag{2}$$

$$2H_2O_2 \leftrightarrows 2H_2O + O_2 \quad \Delta H = -23.7\,kcal \tag{3}$$

All these redox modes have been also observed for peroxo complexes. Frequently, photoredox reactions of metal complexes reflect the electron distribution in the excited states [7]. Accordingly, the oxidation of the peroxide ligand should be preceded by ligand-to-metal (LMCT) excitation while the reduction of O_2^{2-} should be induced by metal-to-ligand (MLCT) excitation. The frontier orbitals of O_2^{2-} (Fig. 1) which are involved are of the π^* type for oxidation and σ^* type for reduction of peroxide. The nature of the reactive state, which initiates the dismutation is less obvious, because an electron transfer between two peroxide ligands must occur.

Of course, these redox reactions are two-electron transfer processes. In contrast, an optical CT transition generally involves one-electron excitation, but it simply indicates a charge shift. There is also evidence that in some cases photoredox reactions of peroxo complexes lead indeed to the generation of stable products such as superoxide, which is formed by one-electron oxidation of peroxide. However, here we will discuss only a few simple reactions, which proceed as two-electron transfer

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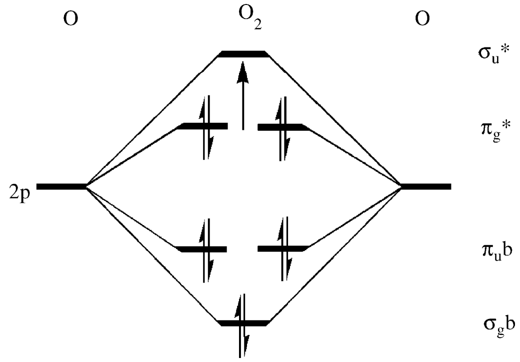


Fig. 1. Qualitative MO scheme for the frontier orbitals of $O_2{}^{2-}$. The arrow indicate the lowest energy $\pi^*\sigma^*$ IL transition.

processes. While product formation conforms to the equations given above the generation of other reactive intermediates is not excluded. Finally, it should be emphasized that the O_2 fragment can not only be coordinated as peroxide, but also as an oxygen molecule or superoxide. Although a clear distinction is not always possible it is useful to apply this classification. While oxygen complexes such as $Pt^0(PPh_3)_2O_2$ [8], or superoxide complexes including $[(NH_3)_5Co^{III}(O_2{}^-)Co^{III}(NH_3)_5]^{5+}$ [2] are also light sensitive, our present discussion is limited to typical peroxo complexes.

2. LMCT excitation

Majority of peroxo complexes contains oxidizing metal centers such as Co(III), Cu(II) or d^0 metals including Ti(IV), V(V) and Cr(VI). Owing to the reducing character of peroxide the electronic spectra of these complexes are dominated by long-wavelength LMCT absorptions, which frequently determine the colours of these compounds [9]. Such colourations serve also as classical spot test for analytical purposes. For example, the blue colour of $Cr^{VI}(O_2)_2O$ (λ_{max} = 580 nm) has been used for the detection of chromium.

Various photochemical studies have been performed with binuclear Co(III) μ-peroxo complexes [1–4]. Upon LMCT excitation of $O_2{}^{2-}$ to Co(III), oxidation of peroxide to oxygen and reduction of Co(III) to Co(II) can take place e.g.:

$$[(\mathrm{trien})Co^{III}(\mu\text{-}OH, O_2)Co^{III}(\mathrm{trien})]^{3+} + 3H_2O + H^+ \xrightarrow{h\nu} 2[Co^{II}(\mathrm{trien})(H_2O)_2]^{2+} + O_2 \quad (4)$$

LMCT excitation of this complex (trien = triethylenetetramine) requires UV irradiation (λ_{irr} = 313 and 365 nm) [10]. Photolysis is not reversible but the reaction can be reversed thermally by addition of oxygen.

We have recently observed an analogous reaction of the $Fe^{III}(\mu\text{-}O_2{}^{2-})Fe^{III}$ moiety [11]. Generally, such complexes are rather unstable. They undergo a facile irreversible conversion to $Fe^{III}(\mu\text{-}O^{2-})Fe^{III}$ complexes. Nevertheless, various labile $Fe^{III}(\mu\text{-}O_2{}^{2-})Fe^{III}$ complexes have been prepared and characterized. Owing to the presence of a long-wavelength $O_2{}^{2-} \rightarrow Fe^{III}$ LMCT absorption (λ_{max} ~500–700 nm) these complexes frequently display a blue colour [12–15].

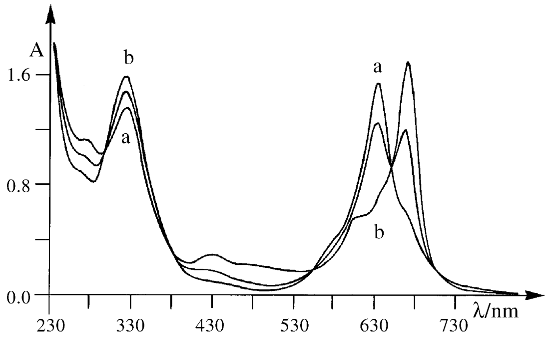
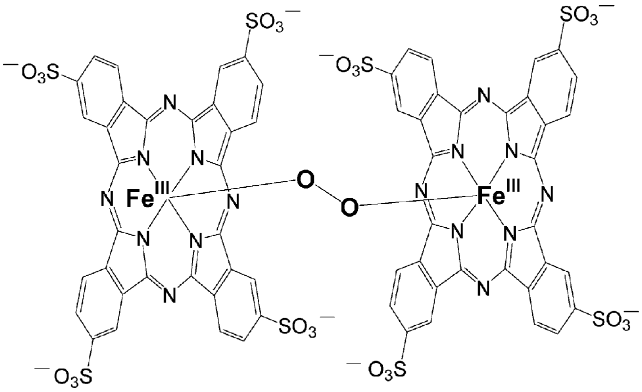


Fig. 2. Spectral changes during photolysis of 5.18×10^{-5} M $(Pcts)Fe^{III}(O_2{}^{2-})Fe^{III}(Pcts)$ in a mixture of water/ethanol (99:1) under argon at room temperature after 0 min (a), 10 and 25 min (b) irradiation times with λ_{irr} = 333 nm (Hanovia Xe/Hg 977 B-1 lamp), 1-cm cell.

We examined the complex $(Pcts)Fe^{III}(O_2{}^{2-})Fe^{III}(Pcts)$ with $PctsH_2$ = phthalocyanine-tetrasulfonate [11].



This complex is formed when $Fe^{II}(Pcts)$ in aqueous solution is exposed to air or oxygen. The binuclear μ-peroxo complex in H_2O persists for some time (~1 h) before it is converted to the μ-oxo complex. Photolysis of the μ-peroxo complex leads to the release of oxygen:

$$(Pcts)Fe^{III}(O_2{}^{2-})Fe^{III}(Pcts) \xrightarrow{h\nu} 2Fe^{II}(Pcts) + O_2 \quad (5)$$

The concomitant spectral changes (Fig. 2) show the same pattern as the formation of the μ-peroxo complex, but in the opposite direction. Under argon photolysis proceeds with $\phi = 5 \times 10^{-4}$ at λ_{irr} = 333 nm. Although it is rather obvious that the photoredox reaction is initiated by $O_2{}^{2-} \rightarrow Fe^{III}$ LMCT excitation, such an assignment is obscured by the spectral properties of the complex. They are dominated by the intraligand (IL) absorptions of the phthalocyanine ligand [16]. In particular, the intense IL bands between 500 and 700 nm prevent the detection of LMCT bands. Since photolysis of $(Pcts)Fe^{III}(O_2{}^{2-})Fe^{III}(Pcts)$ is induced by light absorption in the Pcts IL bands, IL excitation must be followed by the population of a reactive $O_2{}^{2-} \rightarrow Fe^{III}$ LMCT state. Photolysis of various peroxo complexes leads to the release of O_2 in its excited singlet state [6,8,17–19]. This applies apparently also to $(Pcts)Fe^{III}(O_2{}^{2-})Fe^{III}(Pcts)$. In the presence of diphenylacetylene, photolysis leads to the formation of benzil, which is known to be generated by the addition of $^1O_2$ to diphenylacetylene.

As mentioned before, diverse d^0 peroxo complexes are characterized by long-wavelength LMCT absorptions. This applies also to $MeRe(O_2)_2O$ [6]. However, LMCT excitation does not lead to the formation of redox products. In this case, photolysis takes place by a substitution of one peroxide ligand. We suggest that this photolysis reaction proceeds according to the following equations:

$$\mathrm{MeRe^{VII}(O_2{}^{2-})_2O \rightarrow MeRe^{VI}(O_2{}^{2-})O^{+} \ldots O_2{}^{-}}$$

radicalpairformation (6)

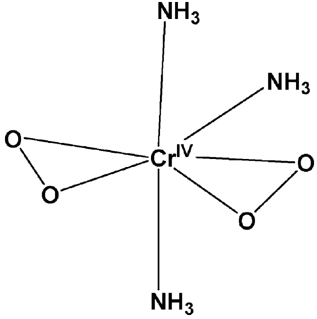
$$\mathrm{MeRe^{VI}(O_2{}^{2-})O^{+} \ldots O_2{}^{-} + H_2O \rightarrow MeRe^{VII}(O_2{}^{2-})O_2 + H_2O_2,}$$

back electron transfer and protonation of $O_2{}^{2-}$ (7)

Generally, LMCT excitation generates a radical pair [7]. This is also valid for Re(VII) complexes including $MeReO_3$ [20]. For $MeRe(O_2)_2O$ the radical pair should be composed of a Re(VI) complex and superoxide. Frequently, radical pairs formed by LMCT excitation undergo a back electron transfer. As a result a photosubstitution may take place. In the present case this step is certainly facilitated by water which protonates the released peroxide and provides the missing oxide ligand for the monoperoxo complex as final photoproduct. In conclusion, the diperoxo complex $MeRe(O_2)_2O$ undergoes a photo-substitution of one peroxide ligand upon low-energy LMCT excitation ($\lambda_{irr} = 405$ nm) [6].

3. MLCT excitation

The complex $Cr(O_2)_2(NH_3)_3$ has been well characterized [21–24]. It contains Cr(IV) coordinated by two peroxide ions.



Since the metal has a d^2 electron configuration ligand field (LF) transitions will be present. They are expected to occur at relatively low energies. Accordingly, the longest wavelength absorption of $Cr(O_2)_2(NH_3)_3$ at $\lambda_{max} = 390$ nm which is relatively weak is assigned to a LF transition [25]. The next band at shorter wavelength ($\lambda_{max} = 257$ nm) is much more intense and assigned to a charge transfer (CT) transition. It may be either of the ligand-to-metal or metal-to-ligand type. Both CT transitions are feasible since Cr(IV) is reducing as well as oxidizing. However, in the case of $Cr(O_2)_2(NH_3)_3$ there is no indication that photolysis affords Cr(III) which should be formed as a stable reduction product. On the contrary, the photochemical generation of $CrO_4{}^{2-}$ is consistent with an MLCT excitation which involves the promotion of a d-electron to the σ^* orbital of peroxide. The absorption of $Cr(O_2)_2(NH_3)_3$ at $\lambda_{max} = 257$ nm which shows the highest photoactivity ($\phi = 0.35$) is assigned to this $d\sigma^*$ ($Cr^{IV} \rightarrow O_2{}^{2-}$) MLCT transition. The quantum yield drops to $\phi = 0.02$ upon irradiation of the LF band at longer wavelength [25].

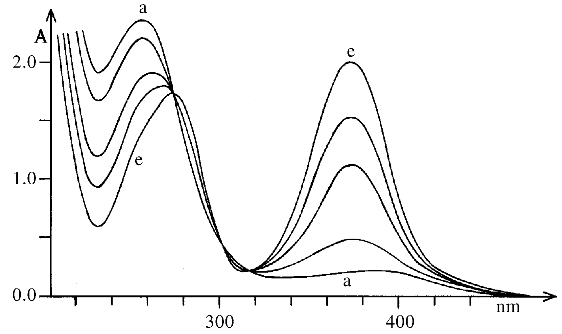


Fig. 3. Spectral changes during photolysis of 4.75×10^{-4} M $Cr^{IV}(O_2)_2(NH_3)_3$ in 0.1 M aqueous NH_3 at 10 °C after 0 s (a), 10, 30, 50 and 100 s (e) irradiation time with white light (Osram HBO 100 W/2 lamp), 1-cm cell.

Photolysis of $Cr(O_2)_2(NH_3)_3$ induced by MLCT excitation can be described by the equation

$$\mathrm{Cr^{IV}(O_2)_2(NH_3)_3 + 2H_2O \rightarrow (NH_4)_2Cr^{VI}O_4 + H_2O_2 + NH_3} \quad (8)$$

The conversion of $Cr(O_2)_2(NH_3)_3$ to $CrO_4{}^{2-}$ is nearly complete as indicated by the spectral variations which accompany photolysis (Fig. 3). Since only one peroxide ligand is involved in the photoredox process the second should be simply released as H_2O_2. This was confirmed by a qualitative analysis.

Photochemical oxidative additions of transition metal complexes have been observed before. However, these reactions are apparently induced by intermolecular excited-state electron transfer processes [7]. In contrast to these reactions the $d\sigma^*$ MLCT excitation of $Cr(O_2)_2(NH_3)_3$ represents the initial step of an oxidative addition which proceeds as an inner-sphere two-electron redox reaction: $Cr^{IV}(O_2{}^{2-}) \rightarrow Cr^{VI}(O^{2-})_2$.

4. IL/LLCT (peroxide) excitation

As mentioned above d^0 peroxo complexes display LMCT bands as longest wavelength absorptions. These assignments are supported by recent calculations on peroxo complexes of Ti(IV) [26], Mo(VI) [27–30] and Re(VII) [30,31] which have shown that the HOMO is largely derived from the occupied π-antibonding orbitals of peroxide while the LUMO contains a considerable d-orbital contribution from the d^0 metal. However, in addition these calculations have led to the conclusion that an empty MO which is essentially based on the σ*-orbital of peroxide is located only at slightly higher energies than the metal-based LUMO. It follows that peroxo complexes of d^0 metals are expected to display peroxide IL $\pi^* \rightarrow \sigma^*$ transitions at accessible energies above the lowest energy LMCT transition. We suggest that this $O_2{}^{2-}$ IL transition belongs to the absorption of $MeRe(O_2)_2O$ at λ_{max} ~260 nm (shoulder) [6]. Similar bands appear also in the spectra of other peroxo complexes such

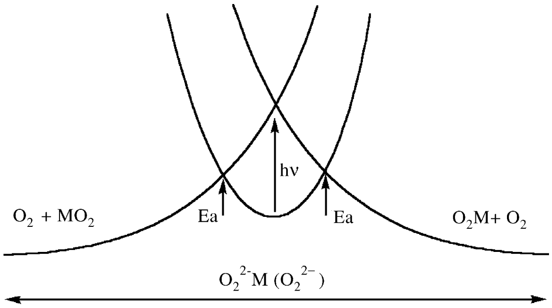


Fig. 4. Qualitative potential energy diagram for the $M(O_2{}^{2-})_2$ fragment of $MeRe(O_2)_2O$.

as $Mo^{VI}(O_2)_2O$ [32] at comparable energies. In distinction to LMCT transitions, IL transitions of this type should be only slightly affected by the metal center. Moreover, the IL $(O_2{}^{2-})$ assignment is in agreement with the photochemical properties of $MeRe(O_2)_2O$.

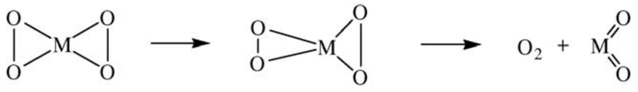
Upon peroxide IL excitation ($\lambda_{max} = 254$ nm) photolysis of $MeRe(O_2)_2O$ in ether essentially proceeds according to the simple equation [6]

$$MeRe^{VII}(O_2)_2O \rightarrow MeRe^{VII}O_3 + O_2 \quad (9)$$

This conclusion is also supported by another observation. The quantum yield for the release of O_2 from $MeRe(O_2)_2O$ increases towards shorter wavelengths and reaches unity at $\lambda_{irr} = 248$ nm [32]. This observation has also led to the suggestion that photolysis is initiated by a higher excited state but its nature has not been discussed.

In a simplified picture, the photochemical changes of $MeRe(O_2)_2O$ induced by IL excitation are restricted to the peroxide ligands: $(O_2{}^{2-})_2 \rightarrow 2O^{2-} + O_2$. While the primary optical transition certainly takes place in the $(O_2{}^{2-})_2$ moiety with equivalent peroxide ligands the subsequent rearrangement is associated with an electron transfer from one peroxide ligand to the other. The $(O_2{}^{2-})_2$ fragment can be viewed as ligand-based mixed-valence (MV) system (Fig. 4) in analogy to certain metal-based MV complexes [33,34]. For example, the binuclear complex $[(NH_3)_5Os^{III}(\mu\text{-}CN)Os^{III}(NH_3)_5]^{5+}$ has been suggested to undergo a light induced disproportionation to Os(II) and Os(IV) [34]. After the initial excitation of $MeRe(O_2)_2O$ (indicated by the vertical arrow) both peroxide ligands are still equivalent, but then the electron density is shifted from one peroxide to the other. Accordingly, the equivalence of both peroxide ligands is lifted. This electron transfer is accompanied by structural changes (e.g. left side of Fig. 3), which finally lead to the dismutation of peroxide (Scheme 1).

The qualitative potential energy diagram (Fig. 4) shows that this reaction can not only be achieved photochemically, but also takes place as a thermal process, which requires an activation energy ($E_a = 14.7$ kcal mol^{-1}) [32].



Scheme 1.

The photodismutation of two peroxo ligands may be a reaction type, which could be of general importance. It has been also observed for $Mo^{VI}(porphyrin)(O_2{}^{2-})_2$ [35]. However, the identification of the reactive excited state is rather difficult in this case since the electronic spectrum of the complex is dominated by the porphyrin IL absorptions.

5. Conclusion

Peroxide complexes undergo photoredox reactions, which can be related to the redox properties of peroxide itself. For complexes with an oxidizing metal center, LMCT excitation leads to the oxidation of peroxide, which may be finally released as molecular oxygen. For complexes with a reducing metal center the electron transfer direction is reversed. MLCT excitation induces the reduction of peroxide to oxide. When two peroxide ligands are coordinated to a metal, peroxide IL excitation can initiate the dismutation to O_2 and $2O^{2-}$.

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