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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.

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

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

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

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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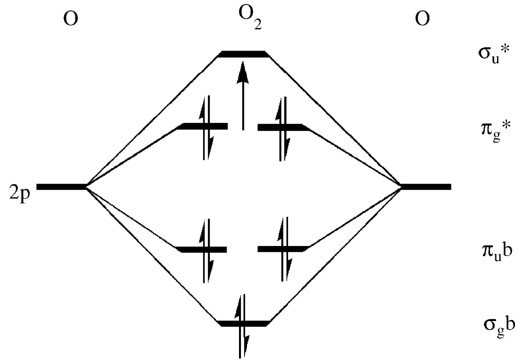


Fig. 1. Qualitative MO scheme for the frontier orbitals of O_2^{2-}. The arrow indicate the lowest energy π*σ* IL transition.

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 $Cr^{VI}(O_2)_2O$ ($\lambda_{max} = 580$ 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.:

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

LMCT excitation of this complex (trien = triethylenetetramine) requires UV irradiation ($\lambda_{irr} = 313$ 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].

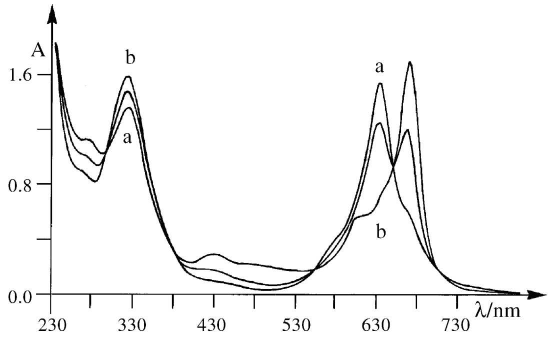
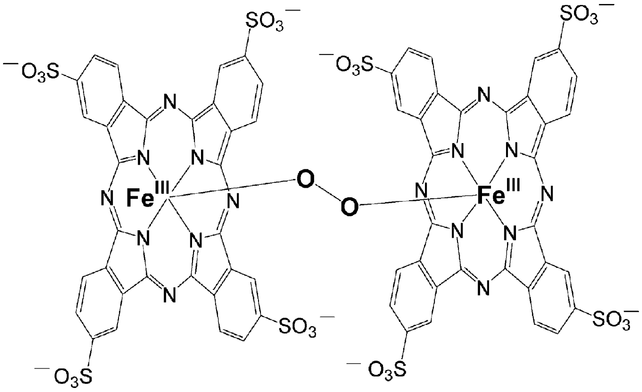


Fig. 2. Spectral changes during photolysis of 5.18×10^{-5} M $(Pcts)Fe^{III}(O_2^{2-})Fe^{III}(Pcts)$ in a mixture of water/ethanol (99:1) under argon at room temperature after 0 min (a), 10 and 25 min (b) irradiation times with $\lambda_{irr} = 333$ nm (Hanovia Xe/Hg 977 B-1 lamp), 1-cm cell.

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 $\lambda_{irr} = 333$ 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.