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Photolysis of $CH_3Re(O_2)_2O$ induced by ligand-to-metal charge transfer and by peroxide intraligand excitation

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Abstract

The electronic spectrum of the diperoxo complex MeRe^{VII}(O₂)₂O shows a peroxide IL (intraligand) absorption at $\lambda_{max} \sim 260$ nm in addition to the well-known peroxide to Re(VII) LMCT band at $\lambda_{max} = 358$ nm. Upon IL excitation, the diperoxo group undergoes a dismutation. Accordingly, MeRe(O₂)₂O photolyzes to MeRe^{VII}O₃ and O₂. LMCT excitation at $\lambda_{irr} = 405$ nm is assumed to generate the radical pair MeRe^{VI}(O₂)O⁺/O⁻₂ in the primary photochemical step. Back electron transfer and reaction with water leads finally to the monoperoxo complex MeRe^{VII}(O₂)O₂ and H₂O₂.

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A variety of peroxo complexes has been shown to be light sensitive [1–10]. The photosensitivity is apparently associated with the peroxo ligand. The nature of the reactive excited states should be related to the chemical properties of peroxide. Since O_2^{2-} is reducing as well as oxidizing, it can serve as CT donor and acceptor, respectively. In combination with an oxidizing metal, LMCT (ligand-to-metal charge transfer) excited states are present at low energies and apparently are responsible for the light sensitivity. When coordinated to a reducing metal, the photolysis may be initiated by MLCT (metal-toligand charge transfer) excitation [5,6]. Finally, peroxide itself has available $\pi^* \rightarrow \sigma^*$ transitions at relatively low energies. We suspected that this $\pi^* \rightarrow \sigma^*$ IL (intraligand) excitation of diperoxo complexes could induce the disproportionation of peroxide.

$$(O_2^{2-})M^{n+}(O_2^{2-}) \rightarrow M^{n+} + 2O^{2-} + O_2 \text{ or } M^{n+}O_2 + O_2$$
(1)

The product formation would finally be the result of an interligand CT process within the $(O_2^{2-})_2$ moiety. The photochemical release of O_2 from complexes such as $Mo^{VI}(O_2)_2O(L)$ [7,8] and $CH_3Re^{VII}(O_2)_2O$ [9,10] may point to such a mechanism. However, the complicated product distribution obscures such a reaction path. Our present study provides some evidence that the peroxide disproportionation initiated by peroxide intraligand excitation of a diperoxo complex indeed occurs.

In agreement with previous reports, we observe that solutions of MeRe(O₂)₂O are light sensitive [9,10]. According to these studies and some general considerations, we expected that MeRe(O₂)₂O, MeReO₃ and HReO₄ are important potential products of the photolysis of MeRe(O₂)₂O. Since the spectra of these complexes are known [9–13], an analysis of the spectral variations which accompany the photolysis may reveal the appearance of these complexes as primary and secondary photoproducts. First of all, we observe that the course of the photolysis of MeRe(O₂)₂O in water-saturated ether depends on the wavelength of irradiation. At $\lambda_{irr} = 254$ nm, the optical density above 300 nm is decreasing proportional to the original extinction

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(Fig. 1). It follows that only MeReO₃ and HReO₄ can be the products since they do not absorb above 300 and 280 nm [13], respectively. In contrast, MeRe(O₂)₂O strongly absorbs at longer wavelength [9,11,12]. During the first stage of the photolysis of $MeRe(O_2)_2O_2$, the original spectrum can be almost completely recovered by treating the photolyzed solution with H_2O_2 . Under our conditions, HReO₄ does not react with H₂O₂ to generate an absorbing peroxo complex such as $H_4Re_2O_{13}$ [14], but MeReO₃ is completely converted to $MeRe(O_2)_2O$ [11,12]. It follows that essentially only MeReO₃ is formed as primary photoproduct upon irradiation of $MeRe(O_2)_2O$ with 254 nm light. However, at later stages of the photolysis, the optical density continues to decrease, but upon addition of H_2O_2 to the photolyzed solution the original spectrum of $MeRe(O_2)_2O$ is only partially recovered. When the photolysis of $MeRe(O_2)_2O$ is driven to completion only HReO₄ is left. Accordingly, HReO₄ is produced as secondary photolysis product by the irradiation of MeReO₃. This photoreaction which takes place in the presence of water is well known [13,15].

At $\lambda_{irr} = 405$ nm, the photolysis of MeRe(O₂)₂O in water-saturated ether takes a different course. The concomitant spectral changes (Fig. 2) show a general decrease of the optical density above 300 nm, but not proportional to the starting extinction at different wavelengths. In particular, the shift of the absorption maximum from 358 to 310 nm (shoulder) is suspicious. These spectral variations are compatible with the formation of MeRe(O₂)₂O₂ ($\lambda_{max} = 310 \text{ nm}$) [11] and MeReO₃. The latter photoproduct does not undergo any secondary photolysis under these conditions because it does not absorb light above 300 nm [13]. Upon addition of H_2O_2 to the photolyzed solution, the starting complex $MeRe(O_2)_2O$ is completely regenerated as indicated by the reversal of the spectral changes. This observation agrees with the chemical behavior of $MeRe(O_2)_2O_2$ and



Fig. 1. Spectral changes during the photolysis of 4.64×10^{-4} M MeRe(O₂)₂O in ether at room temperature after 0 min (a), 10, 20 and 40 min (b) irradiation times with $\lambda_{irr} = 254$ nm (Osram HBO 200 W/2 lamp; Schott monochromatic interference filter UVIL 254), 1 cm cell.



Fig. 2. Spectral changes during the photolysis of 5.85×10^{-4} M MeRe(O₂)₂O in ether at room temperature after 0 min (a), 5, 10 and 25 min (b) irradiation times with $\lambda_{irr} = 405$ nm (Osram HBO 200 W/2 lamp; Schott monochromatic interference filter MA 71 405), 1 cm cell.

MeReO₃. Both complexes are known to form MeRe(O₂)₂O upon addition of H₂O₂ [11,12]. At later stages of the photolysis at $\lambda_{irr} = 405$ nm, the spectral pattern becomes irregular indicating secondary thermal and/ or photochemical reactions which are probably associated with MeRe(O₂)O₂.

Generally, peroxo complexes of d⁰ metals such as Ti(IV), V(V), Cr(VI) and Mo(VI) are characterized by long-wavelength ($O_2^{2-} \rightarrow d^0$ metal) LMCT absorptions which frequently determine the colors of these compounds [16]. There is little doubt that this LMCT assignment applies also to the longest-wavelength bands of MeRe(O₂)O₂ ($\lambda_{max} = 310 \text{ nm}$) and MeRe(O₂)₂O $(\lambda_{\text{max}} = 358 \text{ nm})$ [11]. These LMCT assignments are supported by recent calculations on peroxo complexes of Ti(IV) [17], Mo(VI) [18–21] and Re(VII) [21,22] 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 d⁰ metal. However, in addition these calculations have shown 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(O₂)₂O at $\lambda_{\rm max} \sim 260$ nm (shoulder). Similar bands appear also in the spectra of other peroxo complexes such as Mo^V $(O_2)_2O$ [7] 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 ($\lambda_{max} = 254 \text{ nm}$), the photolysis of MeRe(O₂)₂O in ether essentially proceeds according to the simple equation

(2)

This conclusion is also supported by previous observations. It has been reported that the quantum yield for the release of O₂ from MeRe(O₂)₂O increases towards shorter wavelengths and reaches unity at $\lambda_{irr} = 248$ nm [9]. It is of interest that this observation has also led to the conclusion that the 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 delocalized $(O_2^{2-})_2$ moiety, 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. 3) in analogy to certain metal-based MV complexes [23,24]. After the initial excitation (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. 3) shows that this reaction cannot only be achieved photochemically, but takes also place as an thermal process which requires an activation energy ($E_a = 14.7 \text{ kcal mol}^{-1}$ [9]).

requires an activation energy ($E_a = 14.7 \text{ kcal mol}^{-1}$ [9]). Upon ($O_2^{2-} \rightarrow \text{Re}^{\text{VII}}$) LMCT excitation ($\lambda_{\text{irr}} = 405 \text{ nm}$), the photolysis of MeRe(O_2)₂O in watercontaining ether takes a different course. Since one of the photoproducts is also MeReO₃, it may originate from the IL



Fig. 3. Qualitative potential energy diagram for the $M(O_2^{2-})_2$ fragment of MeRe(O₂)₂O.



Scheme 1.

excited state which could be populated from the initially excited LMCT state by an activated process. However, MeRe(O₂)O₂ as second photoproduct is assumed to be directly generated by LMCT excitation. In this context, it is quite interesting that LMCT excitation of $Mo^{VI}(O_2)_2O$ leads also to the formation of a monoperoxo complex [7]. We suggest that the photolysis of MeRe(O₂)₂O initiated by (O₂²⁻ to Re^{VII}) LMCT excitation proceeds according to the following equation:

$$\begin{split} & \text{MeRe}^{\text{VII}}(\text{O}_2^{2^-})_2\text{O} \to \text{MeRe}^{\text{VI}}(\text{O}_2^{2^-})\text{O}^+ \cdots \text{O}_2^- \\ & \text{radical pair formation} \end{split}$$

$$\begin{split} \text{MeRe}^{\text{VI}}(\text{O}_2^{2-})\text{O}^+ \dots \text{O}_2^- + \text{H}_2\text{O} \\ \rightarrow \text{MeRe}^{\text{VII}}(\text{O}_2^{2-})\text{O}_2 + \text{H}_2\text{O}_2 \end{split}$$

back electron transfer and protonation of O_2^{2-} (4)

Generally, LMCT excitation generates a radical pair [25]. This applies also to Re(VII) complexes including MeReO₃ [13,15,26]. In the case of MeRe(O₂)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 [25]. 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(O₂)₂O undergoes a photosubstitution of one peroxide ligand upon low-energy LMCT excitation ($\lambda_{irr} = 405$ nm). Moreover, shorter-wavelength irradiation at 255 nm leads to peroxide IL excitation which is followed by electron transfer within the (O₂²⁻)₂ ligand fragment. Finally, a dismutation takes place: (O₂²⁻)₂ \rightarrow 2O²⁻ + O₂. As a result, the starting diperoxo complex is photolyzed to MeReO₃.

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