

Photochemistry of the Oxo-bridged Diiron(III) Core. Evolution of Oxygen induced by Fe^{II} to Fe^{III} Charge-transfer Excitation of μ -Oxobis[(ethylenediaminetetraacetato)ferrate(III)]

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The reversible photolysis of aqueous $[\{\text{Fe}^{\text{III}}(\text{edta})\}_2\text{O}]^{4-}$ leads to the evolution of oxygen and the formation of $[\text{Fe}^{\text{II}}(\text{edta})]^{2-}$; it is suggested that the photoreaction is induced by Fe^{II} to Fe^{III} charge-transfer excitation, which yields Fe^{II} and Fe^{IV}=O in the primary photochemical step.

The oxidation of water to oxygen is of fundamental importance in natural and artificial photosynthesis including the cleavage of water into hydrogen and oxygen.^{1,2} Although details of the water oxidation mechanism are not yet known, there is evidence that the oxygen evolving complex of photosystem II contains oxo-bridged manganese clusters as active components.³⁻⁶ In this context we report the photoredox behaviour of the complex anion $[\{\text{Fe}(\text{edta})\}_2\text{O}]^{4-}$. The central Fe^{III}-O-Fe^{III} unit plays a very important role⁷⁻¹⁰ in the biology and chemistry of iron, in general. We conclude that Fe^{III} to Fe^{III} MMCT (metal-to-metal charge transfer) excitation of this group leads to a disproportionation of iron yielding Fe^{II} and Fe^{IV}=O. Two oxoferryl fragments combine to generate Fe^{II} and molecular oxygen. This system represents a simple model for photochemical oxidation of water or oxide.

The absorption spectrum of $\text{Na}_4[\{\text{Fe}(\text{edta})\}_2\text{O}] \cdot 12\text{H}_2\text{O}$ ^{11,12} (Fig. 1) displays bands at $\lambda_{\text{max}} = 405 \text{ nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 120), 342 (1400), 307 (1900), 271 (2400), 245 (2700). In aqueous solution $[\{\text{Fe}(\text{edta})\}_2\text{O}]^{4-}$ partially hydrolyses to $[\{\text{Fe}(\text{Hedta})\}_2\text{O}]^{2-}$.^{11,13} At the complex concentrations used in the photolysis (Fig. 2) a pH of ca. 9 results from this hydrolysis which is associated with slight spectral changes. The absorption bands of the hydrolysed complex appear as shallow features and shoulders (Fig. 2) but hardly change their position. Irradiation of this solution under argon led to the release of dioxygen which was detected qualitatively with an O₂-sensitive electrode at 20 °C (EO 166/k from WTW, Weilheim). In addition, the photolysis was accompanied by spectral changes (Fig. 2) which indicated the production of $[\text{Fe}(\text{edta})]^{2-}$.¹⁴

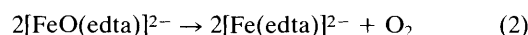
The formation of Fe^{II} was confirmed independently. Upon addition of 1,10-phenanthroline (phen) to the photolysed solution, the red colour of $[\text{Fe}(\text{phen})_3]^{2+}$ ($\lambda_{\text{max}} = 510 \text{ nm}$, $\epsilon = 11500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)¹⁵ developed immediately. The quantum yield for the formation of Fe^{II} was dependent on the wavelength of irradiation (Fig. 1). When the photolysed solution was kept in the dark, $[\{\text{Fe}(\text{edta})\}_2\text{O}]^{4-}$ was regenerated thermally. This process was accelerated if the photolysed solution was exposed to air. The irradiation and regeneration could be repeated several times without a significant loss of

reversibility, provided the extent of each photolysis was limited to less than 25% turnover. After longer irradiation times the reversibility was lost owing to secondary reactions, which may include the irreversible oxidation of the edta ligand.

These observations are consistent with the assumption that the primary photochemical step leads to a disproportionation of the Fe^{III}-O-Fe^{III} moiety, eqn. (1).



The subsequent reaction of two oxoferryl complexes yields Fe^{II} and oxygen; eqn. (2).



Finally, $[\{\text{Fe}(\text{edta})\}_2\text{O}]^{4-}$ can be regenerated by oxidation of $[\text{Fe}(\text{edta})]^{2-}$ with oxygen. The formation of the Fe^{III}-O-Fe^{III} unit by the reaction of Fe^{II} complexes with oxygen in basic solution is of general importance in the chemistry of iron.⁷⁻¹⁰

The disproportionation of the Fe^{III}-O-Fe^{III} group apparently occurs also upon irradiation of the porphyrin complex $[\{\text{Fe}(\text{tpp})\}_2\text{O}]$ [tpp = tetraphenylporphyrinate(2-)].¹⁶ However, in this case, the evolution of oxygen was not observed. Instead, the oxoferryl complex $[\text{Fe}^{\text{IV}}\text{O}(\text{tpp})]$ can be intercepted by various organic compounds. This process has been utilized for photocatalytic oxidations.^{17,18}

According to the wavelength dependence of the quantum yield (Fig. 1), light absorption by the complex at $\lambda_{\text{max}} = 307 \text{ nm}$ is associated with the largest photoactivity. Since a photodisproportionation of Fe^{III} to Fe^{II} and Fe^{IV} is observed, a Fe^{III} to Fe^{III} MMCT transition is a logical assignment. Such an assignment was first suggested by Richman *et al.* who studied the photochemistry of $[\{\text{Fe}(\text{tpp})\}_2\text{O}]$.¹⁶ Unfortunately, the electronic structure and the absorption spectrum of this complex are obscured by the presence of the porphyrin ligand and Richman's ideas of a reactive MMCT state were not generally accepted. Later, the existence of a MMCT state at relatively low energies was also postulated to mediate the antiferromagnetic coupling in the FeOFe⁴⁺ moiety.¹⁹ However, in several studies of the electronic spectra of

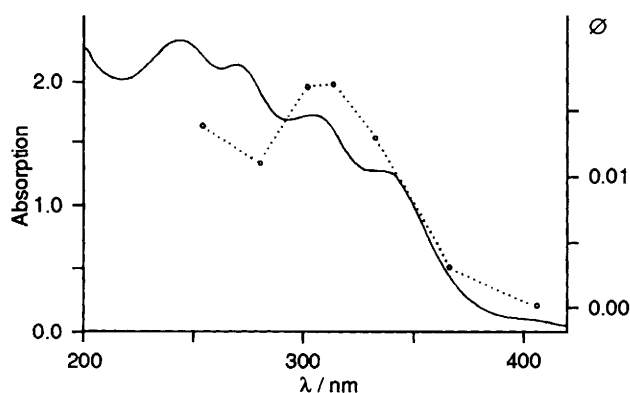


Fig. 1 Electronic absorption spectrum (—) and quantum yield vs. wavelength of irradiation (.....) of $[\{\text{Fe}(\text{edta})\}_2\text{O}]^{4-}$ at room temp. (absorption: $1.74 \times 10^{-1} \text{ mol dm}^{-3}$ solution in H₂O under argon, 0.005 cm cell)

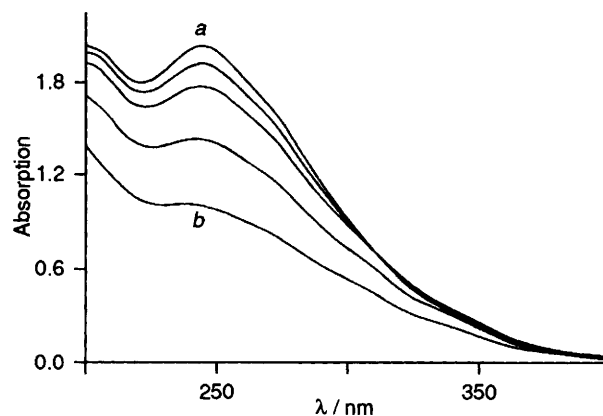


Fig. 2 Spectral changes during the photolysis of $7.55 \times 10^{-3} \text{ mol dm}^{-3}$ $[\{\text{Fe}(\text{edta})\}_2\text{O}]^{4-}$ in H₂O under argon at 0 (a) and 160 s (b) irradiation time, $\lambda_{\text{irr}} = 333 \text{ nm}$ (1 kW Xe-Hg 977 B-1 lamp), 0.1 cm cell

complexes which contain the FeOFe^{4+} group, MMCT transitions were not even considered to occur.²⁰ While the long-wavelength absorptions of $[\{\text{Fe}(\text{edta})\}_2\text{O}]^{4-}$ above 400 nm are of the LF (ligand field) type the so-called 'oxo dimer bands' in the UV region, including the band at $\lambda_{\text{max}} = 342$ nm, were attributed to simultaneous pair excitations,¹¹ or later more conclusively, to oxide to iron^{III} LMCT (ligand to metal charge transfer) transitions.¹² With regard to the photoactivity, both LMCT and MMCT transitions should lead to a disproportionation of the FeOFe^{4+} group and formation of Fe^{2+} and FeO^{2+} . Owing to the strong covalent interaction in the oxoferryl cation there is, however, an ambiguity concerning the oxidation state of iron.²¹ So it is not quite clear if the description of the oxoferryl ion as $[\text{Fe}^{\text{IV}}=\text{O}]^{2+}$ is justified. Nevertheless, the photoactivity of the $\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{III}}$ moiety can be clearly understood on the basis of both assumptions.

Our results are also of considerable interest with regard to the spectroscopy and photochemistry of mixed-valence (MV) compounds. MV complexes are characterized by the presence of the same metal in different oxidation states, in many cases showing low-energy MMCT transitions.²²⁻²⁴ In our case a MV system does not exist in the ground state but is generated by MMCT excitation.

This work was supported by the Bundesministerium für Forschung und Technologie.

Received, 18th July 1994; Com. 4/04387A

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