H. Kunkely and A. Vogler
Institut für Anorganische Chemie, Universität Regensburg, Universitätsstrasse 31, 93040 Regensburg, Germany

The reversible photolysis of aqueous [{Fe(edta)}2O]4− leads to the evolution of oxygen and the formation of [{Fe(edta)}2]2+; it is suggested that the photo reaction is induced by FeIII to FeII charge-transfer excitation, which yields FeII and FeIV=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 [{Fe(edta)}2O]4−. The central FeIII−O−FeIII unit plays a very important role7-10 in the biology and chemistry of iron, in general. We conclude that FeIII to FeII MMCT (metal-to-metal charge transfer) excitation of this group leads to a disproportionation of iron yielding FeII and FeIV=O. Two oxoferryl fragments combine to generate FeII and molecular oxygen. This system represents a simple model for photochemical oxidation of water or oxide.

The absorption spectrum of Na4[{Fe(edta)}2O]12H2O11,12 (Fig. 1) displays bands at λmax = 405 nm (ε/αdm3 mol−1 cm−1 120), 342 (1400), 307 (1900), 271 (2400), 245 (2700). In aqueous solution [{Fe(edta)}2O]4− partially hydrolyses to [{Fe(Hedta)}2]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 evolution of oxygen and the formation of FeII and FeIV=O. Two oxoferryl fragments combine to generate FeII and molecular oxygen. This system represents a simple model for photochemical oxidation of water or oxide.

The absorption spectrum of Na4[{Fe(edta)}2O]12H2O11,12 (Fig. 1) displays bands at λmax = 405 nm (ε/αdm3 mol−1 cm−1 120), 342 (1400), 307 (1900), 271 (2400), 245 (2700). In aqueous solution [{Fe(edta)}2O]4− partially hydrolyses to [{Fe(Hedta)}2]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 intercept 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 λmax = 307 nm is associated with the largest photoactivity. Since a photodisproportionation of FeIII to FeII and FeIV is observed, a FeIII to FeII MMCT transition is a logical assignment. Such an assignment was first suggested by Richman et al. who studied the photochemistry of [{Fe(tpp)}2]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 postulated to mediate the antiferromagnetic coupling in the FeOFeII moiety.19 However, in several studies of the electronic spectra of
complexes which contain the FeOFe4+ group, MMCT transitions were not even considered to occur. While the long-wavelength absorptions of \([\{\text{Fe(edta)}\}]\text{O}^{4-}\) above 400 nm are of the LF (ligand field) type the so-called ‘oxo dimer bands’ in the UV region, including the band at \(\lambda_{\text{max}} \approx 342\) nm, were attributed to simultaneous pair excitations, or later more conclusively, to oxide to iron\[^{\text{III}}\] LMCT (ligand to metal charge transfer) transitions. With regard to the photoactivity, both LMCT and MMCT transitions should lead to a disproportionation of the FeOFe4+ group and formation of Fe2+ and FeO*. Owing to the strong covalent interaction in the oxoferryl cation there is, however, an ambiguity concerning the oxidation state of iron. So it is not quite clear if the description of the oxoferryl ion as \([\text{FeIV=O}]^{*+}\) is justified. Nevertheless, the photoactivity of the Fe2+-O-Fe2+ 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. 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. 40/4387A

References