A Labile Product in the Photoreduction of Tetrakis-(1,10-phenanthroline)-diaquo-μ-oxo-di-iron(III)

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Summary Photoreduction of tetrakis-(1,10-phenanthroline)-diaquo-μ-oxo-di-iron(III) in aqueous medium to form $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) seems to continue even after cessation of irradiation; kinetic evidence supports the formulation of a thermally labile peroxo-bridged binuclear complex, which undergoes thermal reduction and rearrangement to $[Fe^{II}(phen)_3]^{2+}$.

The primary process in the photoreduction of tetrakis-(1,10-phenanthroline)diaquo-μ-oxo-di-iron(III) in aqueous medium is homolytic cleavage of Fe–O "bridge" bond.[1,2]

$$\underset{\text{(I)}}{[(phen)_2(H_2O)Fe^{III}\text{–O–}Fe^{III}(H_2O)(phen)_2]^{4+}} \xrightarrow[350\ \text{nm}]{h\nu}$$

$$\underset{\text{(II)}}{[(phen)_2(H_2O)Fe^{II}]^{2+}} + \underset{\text{(III)}}{[\cdot O\text{–}Fe^{III}(H_2O)(phen)_2]^{2+}} \qquad (1)$$

The primary fragment (II) undergoes rapid rearrangement[2,3] in aqueous medium to $[Fe(phen)_3]^{2+}$, but nothing is known about the behaviour of the radical cation (III). I report here evidence for the formation of a thermally labile product, possibly formed by the dimerization of (III).

An aqueous solution of (I) is thermally stable for several days even at 50 °C, but photoreduction of (I) seems to continue for several days at room temperature even after cessation of the u.v. irradiation ('dark reduction'). This could be due to thermal reduction of Fe^{3+}(aq.), one of the final products in the photoreduction of (I),[2] and its subsequent reaction with (I). However, (I) is not reduced in the presence of further $FeCl_3$ and the dark reduction still takes place in the presence of additional phen, which would rapidly co-ordinate to Fe^{3+} or Fe^{2+}. Radical reduction of (I) (*e.g.* by ·OH or ·Cl) may be ruled out, since such radicals are not detected during the photoreduction of (I).[1,2] This evidence indicates strongly that the dark reduction is due to fragment (III).

The dark reduction follows first-order kinetics (k 1·85 × $10^{-5}\ s^{-1}$ at 30 °C; E_a 17 ± 2 kcal). The rate of formation of $[Fe(phen)_3]^{2+}$ is independent of the initial concentration of (I) or its concentration after cessation of irradiation.† It is interesting that the rate of the dark reduction depends only on the concentration of (I) that has undergone photoreduction. I suggest that the dark-reduction is due to thermal reduction of the peroxo-bridged compound (IV), formed by the dimerization of the radical cation (III).

The observed ratio of the concentration of $[Fe(phen)_3]^{2+}$ immediately after cessation of irradiation to that produced

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† Compound (I) (10^{-3}—10^{-4} M) was irradiated in a Rayonet Photochemical Reactor for 5—10 min and the rate of production of $[Fe(phen)_3]^{2+}$ was studied. Percentage conversions immediately after irradiation were in the range 2—20%.

$$\underset{\text{(III)}}{2\,[(\mathrm{phen})_2(\mathrm{H_2O})\mathrm{Fe^{III}}\text{–}\mathrm{O}\cdot]^{2+}} \xrightarrow{\text{fast}} \underset{\text{(IV)}}{[(\mathrm{phen})_2(\mathrm{H_2O})\mathrm{Fe^{III}}\text{–O–O–}\mathrm{Fe^{III}}(\mathrm{H_2O})(\mathrm{phen})_2]^{4+}} \qquad (2)$$

$$\text{(IV)} \xrightarrow{k} 2\,[(\mathrm{phen})_2(\mathrm{H_2O})\mathrm{Fe^{II}}]^{2+} + \mathrm{O_2} \qquad (3)$$

by the dark reduction is unity, consistent with formation of the labile peroxo-bridged compound (IV).

Photoreduction of (I) in methanol shows no dark-reducrion. It is known that homolytic cleavage of the Fe–O 'bridge' bond is not the primary process in the photoreduction of (I) in methanol,[4] additional evidence that the dark reduction involves the radical cation (III).

Surprisingly, there is no spectral evidence for the formation of (IV), but it may have an electronic absorption spectrum similar to that of (I), and so would not have been detected.

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