

Iron *meso*-Tetra(2,6-dichlorophenyl)porphyrin as a very Efficient Catalyst for the Photoreduction of Carbon Tetrachloride by Alcohols

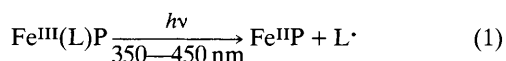
Carlo Bartocci,^{a*} Andrea Maldotti,^a Graziano Varani,^a Vittorio Carassiti,^a Pierrette Battioni,^b and Daniel Mansuy^b

^a Centro di Fotochimica del CNR, Dipartimento di Chimica dell'Università di Ferrara, Via L. Borsari, 46 I-44100 Ferrara, Italy

^b Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, UA 400 CNRS, Université René Descartes, 45 rue de Saints Pères, F-75270 Paris Cédex 06, France

The ability of Fe(tdcpp)(Cl), iron *meso*-tetra(2,6-dichlorophenyl)porphyrin chloride, to act as an efficient catalyst for photoredox reactions is shown by both the unusually high Fe^{III} photoreduction quantum yield and the high recycle numbers obtained in the catalytic photoreduction of carbon tetrachloride by alcohols.

Several authors¹ have demonstrated that non-emitting iron porphyrin (FeP) complexes undergo intramolecular redox photochemistry according to reaction (1). If, after photoreduction, the Fe^{III} porphyrin reactant can be regenerated, a catalytic cycle should result in which Fe^{II} and L· are capable of inducing reactions on organic substrates.² The interest in these processes is growing in view of their relevance to homogeneous catalysis and biomimetic chemistry.



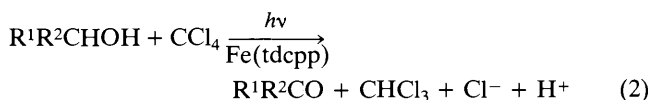
There are two main obstacles to this, however: the low values of the Fe^{III} photoreduction quantum yields in the absence of Fe^{II} quenchers, and the low stability of the porphyrin ring with respect to degradation.

Herein, we examine the photoredox behaviour of the electronegatively substituted iron *meso*-tetra(2,6-dichlorophenyl)porphyrin chloride, Fe(tdcpp)(Cl), which has been found to be resistant towards oxidative degradation and appears to be a good oxidation catalyst.³ Its use in the catalytic photoreduction of CCl₄ by alcohols led to a considerable improvement in turnover compared with those previously obtained with iron octaethylporphyrin chloride, Fe(oep)(Cl).^{2c}

Irradiation at 350–450 nm of Fe^{III}(tdcpp) (2 × 10⁻⁵ mol dm⁻³) was carried out in carefully deaerated ethanol or propan-2-ol solutions.† Previous work^{1a,b,f} indicated that in those solvents the photoreactive species was an Fe^{III} porphyrin containing an alcoholate molecule axially bound to iron. According to the general photoreduction mechanism,^{1a} the u.v.-vis. spectral changes observed during the photochemical experiments indicated that the irradiation led to a clean reduction of Fe^{III}(tdcpp) to Fe^{II}(tdcpp). Irradiation in an e.s.r. cavity in the presence of phenyl-*t*-butylnitron, PBN,^{1f} a species capable of trapping radicals to give stable paramagnetic nitroxides,⁴ gave clear evidence that an alkoxy radical⁵ was formed in the primary photochemical act.‡ The quantum yields at 365 ± 5 nm for the formation of Fe^{II}(tdcpp) were 2.5 × 10⁻² in ethanol and 4.5 × 10⁻² in propan-2-ol. When identical experiments were performed with iron-*meso*-tetraphenylporphyrin chloride, Fe(tpp)(Cl), or Fe(oep)(Cl), no

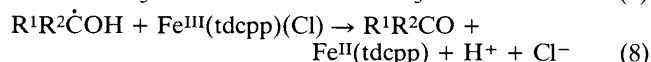
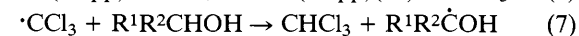
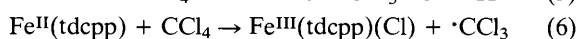
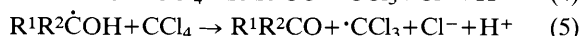
appreciable e.s.r. signals were observed and very low photoreduction quantum yields, *i.e.*, 5 × 10⁻³ and 10⁻³, respectively, were obtained.

Since the products of the primary photochemical reaction, Fe^{II}(tdcpp) and an alkoxy radical, are able effectively to react with CCl₄ *via* electron-transfer processes, photolysis of Fe^{III}(tdcpp) is expected to initiate the catalytic reduction of CCl₄ to CHCl₃ and Cl⁻. Indeed, when deaerated alcohol solutions of Fe(tdcpp)(Cl) were irradiated in the presence of CCl₄, the catalytic reaction (2) occurred, as shown by the g.l.c. detection of CHCl₃ and potentiometric measurement of Cl⁻,^{2c}



with R¹ = Me and R² = H or $\bar{\text{C}}\text{H}_2$.

Fe^{III}(tdcpp) and R¹R²CHO· can be considered as the initiators of the chain process. The successive chain propagation steps (reactions 3–8) explain the observed formation of R¹R²CO, CHCl₃, and Cl⁻.§



The re-oxidation of Fe^{II}(tdcpp) by CCl₄ was investigated by laser-flash photolysis (Applied Photophysics detection system coupled with a J.K. system 2000 frequency doubled ruby laser, delivering 25 ns pulses of 347 nm radiation). From the mono-exponential decay curves observed at 430 nm, corresponding to the Soret band of Fe^{II}(tdcpp), a pseudo-first-order constant of (5 ± 1) × 10⁶ s⁻¹ was obtained.

The results obtained with irradiation in the range 350–450 nm¶ are reported in Table 1. All the experiments were carried out in carefully deaerated solution because oxygen removed the chain carriers R¹R²ĊOH and ·CCl₃ in the photocatalytic process by reacting with them. In the absence of oxygen, Fe(tdcpp)(Cl) was found to be very stable, allowing high recycle numbers (moles of Cl⁻ formed per mole of consumed iron porphyrin catalyst).

§ The formation of R¹R²CO was demonstrated by gas chromatography with an 80–100 mesh Chromosorb-102 column. Cl⁻ was analysed by potentiometry.

¶ During this time 2 × 10⁻³ moles of photons were estimated to be absorbed by the porphyrin solution.

† Irradiation was carried out at room temperature with a Hanau Q 400 medium-pressure mercury lamp, equipped with glass optical filters. The solutions were previously degassed to less than 10⁻⁵ mmHg by means of five vacuum line freeze-thaw pump cycles.

‡ The e.s.r. signals were typical of an adduct of PBN with the CH₃CH₂O· radical (*a*_N 14.5 G; *a*_H 2.6 G) and with (CH₃)₂CHO· (*a*_N 14.5 G; *a*_H 2.3 G) (*G* = 10⁻⁴ T).

Table 1. Characteristics of the photo-assisted reduction of CCl₄ by alcohols, catalysed by iron porphyrins.

Catalyst (5 × 10 ⁻⁵ mol dm ⁻³)	Substrate, CCl ₄ (mol dm ⁻³)	Solvent	Cl ⁻ formed (mol dm ⁻³)	Consumed catalyst (%)	Recycle ^a number
Fe(tdcp)(Cl) ^b	1.0	EtOH	2.0 × 10 ⁻²	<2	>20 000
Fe(tdcp)(Cl) ^b	0.05	EtOH	8.0 × 10 ⁻³	<2	>8 000
Fe(tpp)(Cl) ^c	1.0	EtOH	4.0 × 10 ⁻⁴	~25	~32
Fe(tdcp)(Cl) ^b	1.0	Pr ⁱ OH	1.3 × 10 ⁻¹	<2	>130 000
Fe(oep)(Cl) ^d	1.0	EtOH	5.0 × 10 ⁻³	~100	~100

^a Moles of Cl⁻ formed per mole of consumed catalyst. ^b 20 h irradiation at λ>350 nm in deaerated solution. ^c 1 h irradiation at λ>350 nm in deaerated solution. ^d 2 min irradiation at λ>350 nm followed by 2 h in the dark at 25°C in the presence of 1 mmHg of oxygen (see ref. 2c).

The quantum yield and recycle numbers were also high at a low initial concentration of CCl₄. The fact that propan-2-ol is more efficient than ethanol in reducing CCl₄ is in agreement with the known higher oxidation potential of the hydroxypropyl radical than that of hydroxyethyl radical.⁶

The high photocatalytic activity is a peculiarity of Fe(tdcp). Identical experiments performed with the parent Fe(tpp) compound led to no more than 200 recycles because the iron porphyrin catalyst was completely decomposed in less than 120 min (Table 1).

The catalytic efficiency of Fe(tdcp) is also higher than that of Fe(oep), which, under comparable conditions, catalyses the photoreduction of CCl₄ with much lower recycle numbers (Table 1) because of its low stability.

The observed stability of Fe(tdcp) could depend on the steric hindrance as well as the electronegativity of the eight chlorine atoms. Their function, in any case, should be to prevent the attack by radical intermediates on the *meso* positions of the porphyrin ring.

More detailed studies are clearly needed to determine precisely the role played by the peripheral substituents. For this purpose we intend to investigate the photocatalytic behaviour of protected iron porphyrins other than Fe(tdcp), in the reduction of CCl₄ and other halogenated alkanes by alcohols.

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