# Photochemical Cleavage of 1,2-Diphenylethane-1,2-diol by Water-soluble $Fe^{III}$(tmpyp) {$Fe^{III}$(tmpyp) = [*meso*-tetrakis(1-methyl-4-pyridinio)porphyrinato]iron(III)}

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Visible-light photolysis of 1,2-diphenylethane-1,2-diol and $Fe^{III}$(tmpyp) in argon-saturated 50% aqueous MeCN afforded benzaldehyde and $Fe^{II}$(tmpyp) in a stoichiometric manner, and in the presence of air, benzaldehyde was photocatalytically produced with concomitant formation of benzoic acid as a minor product; turnover numbers and quantum yields strongly depended on the solution pH, virtually no reaction occurring at pH 2.

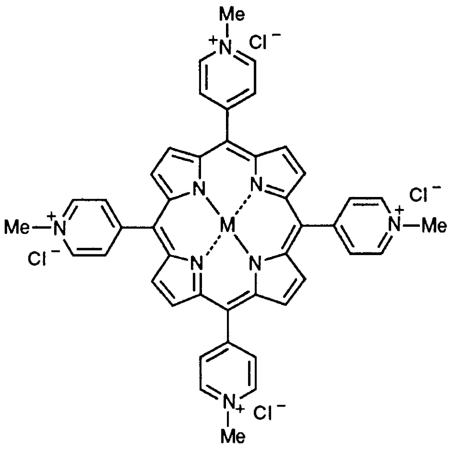
The photochemistry of porphyrins and metalloporphyrins is important in view of their potential applications to artificial photosynthesis and photodynamic therapy of cancer.[1] For example, the water-soluble *meso*-tetrakis(1-methyl-4-pyridinio)porphyrin, $H_2$tmpyp, and its metal complexes have been used to split water[2] or to cleave DNA.[3] However, organic reactions photocatalysed by metalloporphyrins with a redox-active central metal are still rare. Recently there has been increasing interest in organic reactions carried out in aqueous solution. Here I describe the C–C bond cleavage of 1,2-diphenylethane-1,2-diol **1** caused by $Fe^{III}$(tmpyp).

Visible-light photolysis (>400 nm) of an MeCN–$H_2O$ (1 : 1 v/v) solution containing $1.3 \times 10^{-4}$ mol dm$^{-3}$ $Fe^{III}$(tmpyp)[4] and $9.4 \times 10^{-3}$ mol dm$^{-3}$ *meso*-**1** was carried out in a closed UV cell under argon atmosphere at pH 6.2 (before irradiation). As displayed in Fig. 1, reduction of $Fe^{III}$(tmpyp) ($\lambda_{max}$ 420 nm) to $Fe^{II}$(tmpyp) ($\lambda_{max}$ 442 nm) with five isosbestic points, and formation of about one equivalent of benzaldehyde, which was confirmed by HPLC analyses, were rapidly effected (eqn. 1). From this point, essentially no further spectral changes were observed on further irradiation. However, introduction of air or oxygen into the cell readily resulted in complete disappearance of $Fe^{II}$(tmpyp), with recovery of $Fe^{III}$(tmpyp) in 95% yield, while a slight increase in the yield of benzaldehyde was detectable. In a separate experiment, the quantum yield ($\phi$) for the $Fe^{II}$(tmpyp) formation was estimated as 0.016 at pH 7.0. The reaction strongly depended on the solution pH, adjusted with HCl and NaOH. Thus, it was extremely slow at pH 2 with $\phi$ for $Fe^{II}$(tmpyp) *ca.* 0.0005, which increased with pH, reaching a maximum value (0.016) at pH 7, and then decreased to 0.010 at pH 12, although $Fe^{II}$(tmpyp) produced was unstable to light at pH 12.

When the photolysis was done with bubbling argon, benzaldehyde was produced catalytically. After prolonged irradiation, nearly all the porphyrin catalyst decomposed (from UV–VIS) and the reaction stopped. Probably, traces of oxygen in the argon stream are responsible for cycling the porphyrin catalyst. Selected data are listed in Table 1. Product yields were determined by HPLC analyses. When both the concentration of *meso*-**1** and the solution pH are high, the yield of benzaldehyde on the basis of the porphyrin catalyst reached 19000% (run 4), *i.e.* turnover number = 190.

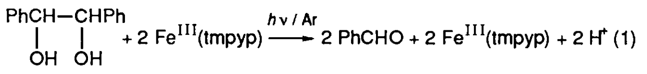
When the photolysis was done under air rather than with argon bubbling, benzaldehyde formation and catalyst decomposition proceeded much faster (runs 2, 3 and 5) and a substantial amount of benzoic acid was produced as an additional product (runs 2 and 3). Owing to this fast catalyst decomposition, the product yields were lower under air than with argon bubbling: compare run 1 with run 2 and 4 with run 5. The product yields were even lower with oxygen bubbling. Probably, certain peroxidic species derived from the oxygen molecule are destroying the porphyrin catalyst. It is also apparent from Table 1 that appreciable lowering of pH was always observed after irradiation.

As just mentioned, $\phi$ for $Fe^{II}$(tmpyp) was dramatically influenced by pH. The same was true for $\phi$ values for PhCHO and $PhCO_2H$. As is evident from Fig. 2, where relative quantum yields ($\phi_{rel}$) for production of PhCHO and $PhCO_2H$ under air are plotted against the pH of the solution (before irradiation), virtually no reaction occurred around pH 2. While $\phi$ for PhCHO increased linearly from pH 2 to pH 12, formation of benzoic acid was again suppressed above pH 11. Absolute quantum yields were estimated as 0.059 (for PhCHO) and 0.013 (for $PhCO_2H$) at pH 7.2 for $1.3 \times 10^{-4}$ mol $dm^{-3}$ Fe(tmpyp) and $9.4 \times 10^{-3}$ mol $dm^{-3}$ *meso*-**1**. When the reaction was done at a higher pH (10.6) and a higher concentration of *meso*-**1** ($4.7 \times 10^{-2}$ mol $dm^{-3}$), the quantum yields reached 0.20 (for PhCHO) and 0.027 (for $PhCO_2H$). Although these quantum yields are also affected by the concentration of Fe(tmpyp) ($1.3–13 \times 10^{-4}$ mol $dm^{-3}$) and by that of externally added NaCl ($0–12 \times 10^{-3}$ mol $dm^{-3}$), their effects were definitely not so large as the effect of either the solution pH or the concentration of **1** mentioned above.



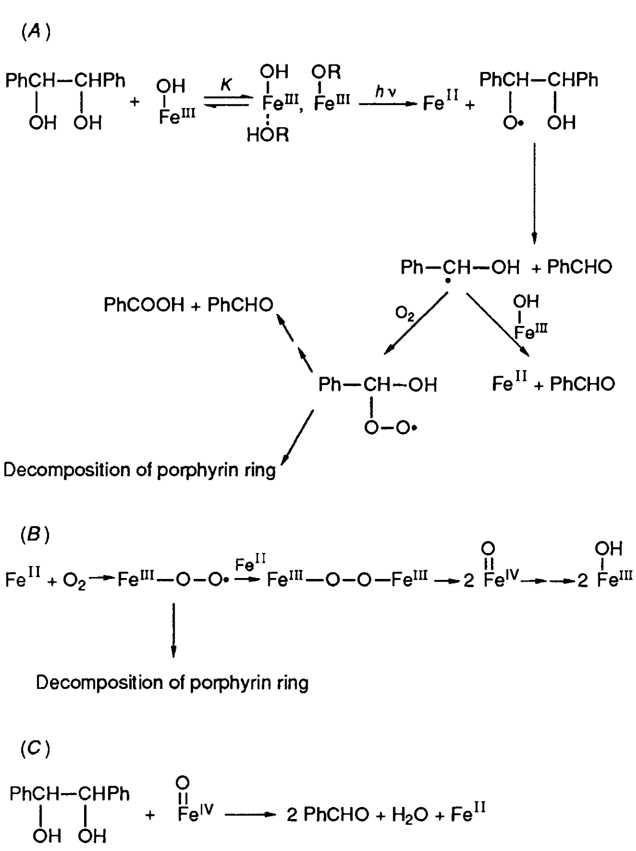
M = $Fe^{III}Cl$

$Fe^{III}(tmpyp)Cl_5$



$$PhCH(OH)-CH(OH)Ph + 2\,Fe^{III}(tmpyp) \xrightarrow{h\nu / Ar} 2\,PhCHO + 2\,Fe^{III}(tmpyp) + 2\,H^+ \quad (1)$$

**1**



**Scheme 1**

**Table 1** Photocleavage of the diol **1** by $Fe^{III}$(tmpyp) in MeCN–$H_2O$ (1:1 v/v): $h\nu$, $\lambda > 400$ nm, $[Fe^{III}(tmpyp)] = 1.3 \times 10^{-4}$ mol $dm^{-3}$

| Run | Substrate | pH[a] | Atmosphere | Irradn. time/h | Products (%)[b] | | Recovered porphyrin |
|---|---|---|---|---|---|---|---|
| | | | | | PhCHO | $PhCO_2H$ | |
| 1 | *meso*-**1**[c] | 7.4 (5.5) | Ar[e] | 40 | 5000 | 0 | Trace |
| 2 | *meso*-**1**[c] | 7.4 (5.0) | Air | 12 | 2100 | 350 | None |
| 3 | (±)-**1**[c] | 7.2 (4.8) | Air | 12 | 2100 | 380 | None |
| 4 | *meso*-**1**[d] | 12.6 (9.6) | Ar[e] | 60 | 19000 | Trace | Trace |
| 5 | *meso*-**1**[d] | 12.3 (9.0) | Air | 4 | 7800 | Trace | None |

[a] Before irradiation; pH after irradiation is in parentheses. [b] (product/cat.) × 100. [c] [**1**] = $9.4 \times 10^{-3}$ mol $dm^{-3}$. [d] [**1**] = $4.7 \times 10^{-2}$ mol $dm^{-3}$. [e] Argon bubbling.

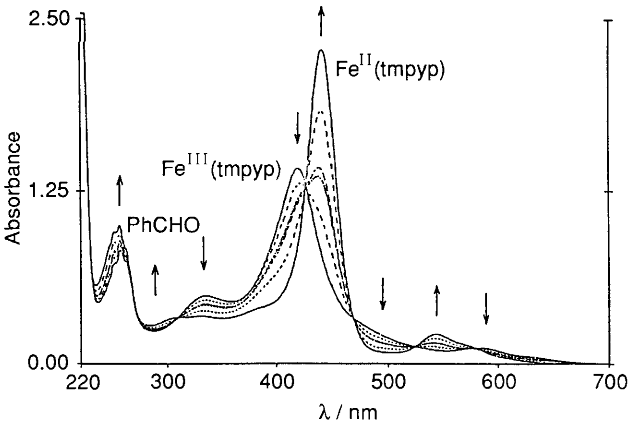


**Fig. 1** Spectral changes of a mixture of $1.3 \times 10^{-4}$ mol dm$^{-3}$ Fe$^{III}$(tmpyp) and $9.4 \times 10^{-3}$ mol dm$^{-3}$ *meso*-**1** in Ar-saturated MeCN–$H_2O$ (1 : 1 v/v) at pH 6.2 upon photolysis (>400 nm); pathlength, 1 mm. The spectra were taken at t = 0, 1, 2, 3, 4.5 and 9.5 min.

A plausible mechanism for the above reactions is outlined in Scheme 1*A*–*C*.

Fe$^{III}$(tmpyp) appears to exist mainly as monomeric aqua or hydroxo complexes in water.[5] Involvement of a μ-oxo dimer as a photoreactive species was neglected, since photocatalytic cleavage of *meso*-**1** by the cofacially hindred [*meso*-tetrakis(3,5-dichloro-1-methyl-4-pyridinio)porphyrinato]iron(III), Fe$^{III}$(tclmpyp)[6], depended on pH in just the same manner as in Fig. 2. The μ-oxo dimerization of Fe(tclmpyp) is thought to be sterically hindered.[6] Slight changes in the absorption spectrum of Fe$^{III}$(tmpyp) observed upon addition of *meso*-**1** indicate some intermolecular interactions between them. Reduction of Fe$^{III}$ by an axially coordinated alcohol has previously been suggested.[7] Similar coordination is probably crucial for the present photoreaction to occur, since the excited states of Fe$^{III}$(tmpyp) will be very short-lived.[8]

The concomitant formation of benzoic acid under air supports the radical mechanism proposed in Scheme 1*A*, where $O_2$ and Fe$^{III}$(tmpyp) compete for trapping the benzaldehyde ketyl radical. Reduction of iron(III) to iron(II) porphyrins by a ketyl radical is common.[7,9] Schemes 1*A* and 1*B* can well explain the observed contradictory role of the oxygen molecule, *i.e.* $O_2$ is required for turnover of the catalyst,[18] but impairs product yields at high concentrations by destroying the catalyst.

Scheme 1*C* is considered, because the combined φ value for PhCHO and $PhCO_2H$ (0.072 under air) was much larger than the φ value for Fe$^{II}$(tmpyp) (0.016 under argon). Cleavage of 1,2-diols by oxo–metal porphyrin complexes has previously been reported.[11] Furthermore, I found that, although φ for Fe$^{II}$(tmpyp) (under argon) did not depend on the concentration of *meso*-**1** ([**1**] = 0.01–0.05 mol dm$^{-3}$), φ for PhCHO (under air) did ([**1**] = 0.005–0.05 mol dm$^{-3}$). The latter finding also requires Scheme 1*C*. The former finding suggests a large association constant *K* between **1** and Fe$^{III}$(tmpyp).

The observed strong inhibition of the reaction around pH 2 is likely owing to preferential coordination of $Cl^-$ ions to Fe$^{III}$, obstructing the coordination of the diol. The increase in φ for PhCHO at higher pH may indicate that Scheme 1*C* becomes more effective at higher pH.

The photocatalytic cleavage of other 1,2-diols such as 1-phenylethane-1,2-diol **2**, 2,3-dimethylbutane-2,3-diol **3**, and 1,1,2,2-tetraphenylethane-1,2-diol **4** as well as benzoin **5** likewise occurred with argon bubbling or under air: **4** was cleaved even in the dark and **5** afforded benzaldehyde and benzoic acid in equal amounts. In contrast to Fe$^{III}$(tmpyp), chloro(*meso*-tetraphenylporphyirinato)iron(III) was unable to photosensitize the C–C bond cleavage for **1**, **2** and **5** in aerated methylene chloride.

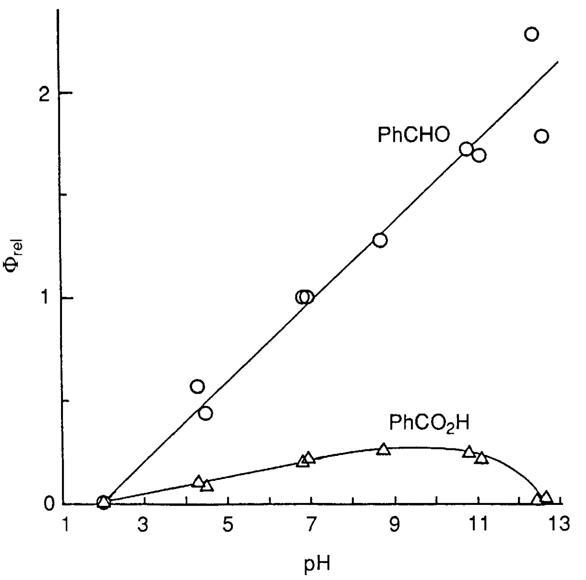


**Fig. 2** Relative quantum yields for photocleavage of *meso*-**1** in aerated MeCN–$H_2O$ (1 : 1 v/v) at various pH (HCl or NaOH): [Fe$^{III}$(tmpyp)] = $1.3 \times 10^{-4}$ [*meso*-**1**] = $9.4 \times 10^{-3}$ mol dm$^{-3}$

*Received, 30th October 1990; Com. 0/04877A*

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