

Experimental Section

Materials. Acetonitrile was obtained from Fisher Scientific and distilled over P_2O_5 prior to use. *m*-CPBA (77%) purchased from Aldrich Chemical Co. was purified by crystallization in methylene chloride and then dried in vacuum. Iodosobenzene was purchased from the TCI America Co. and used as such. All reactive substrates for LFP kinetic studies and catalytic competition oxidations were the best available purity from Aldrich Chemical Co. and passed through a dry column of active alumina (Grade I) before use. $Mn^{III}(TPFPP)(Cl)$ was prepared according to the literature procedure and purified by chromatography on silica-gel column. $Mn^{III}(TPP)(Cl)$ and $Mn^{III}(TMPyP)(Cl)$ were obtained from Aldrich Chemical Co. and Mid-Century Chemicals, respectively, and used without further purification. All perchlorate salts of manganese(III) porphyrin complexes were prepared by stirring equimolar amounts of the $Mn^{III}(Porph)(Cl)$ with $AgClO_4$ salt followed by filtration. The resulting solution was used for LFP study immediately. $Mn^{III}(TPFPP)(NO_3)$ was also prepared in a similar way.

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

Instrumentation. UV-vis spectra were recorded on an Agilent 8453 spectrophotometer. Laser flash photolysis was conducted on an LK-60 kinetics spectrometer (Applied Photophysics) at ambient temperature (ca. 22 ± 2 °C). Stock solutions of manganese(III) perchlorate porphyrin complexes with a concentration of $7.0 - 8.0 \times 10^{-6}$ M were sparged with helium and then allowed to flow through a 1×1 cm quartz cell. Samples were irradiated with 355 nm light from a Nd-YAG laser (2 to 7 ns pulse). Data were acquired and analyzed with the Applied Photophysics software. Oversampling (64:1) was employed in all cases to improve the signal to noise.

The stopped-flow study of the stoichiometric reaction between $Mn^{III}(TMPyP)(Cl)$ (5 μ M) and *m*-CPBA (15 μ M) was performed by single mixing on a RX2000 rapid kinetics spectrometer accessory (Applied Photophysics) coupled with an Agilent 8453 UV-vis spectrophotometer using fast-scan mode. The concentrations listed here were the final concentrations after mixing. The scan time was 40 s with 1 s integration time for the photodiode array, and only eight scans are shown in Figure 3.

Reactions of manganese perchlorate salts and *cis*-stilbene were performed in a Rayonet photoreactor with a low pressure mercury lamp (300-400 nm) for 24 h at 30 °C, and the ratio of *cis*- and *trans*-epoxide was determined by 1H NMR (Varian Mercury-Vx-300) with 1% TMS as internal standard.

LFP Kinetics. The decay rates of manganese(V)-oxo intermediates in the presence of reactive substrates were directly measured at 432 (**2**), 435 (**4**) and 450 (**6**) nm, respectively, in acetonitrile solution. The kinetic profiles exhibited a double exponential process. Detailed rate constants (k_1 and k_2) are listed in Table S1. The slow decay process was not altered by the addition of substrates, and we do not know the origin of this slow decay process.

The efficiencies of the LFP reactions were evaluated qualitatively with the assumption that all Mn^V -oxo species have the same molar absorbances. Reactions in CH_3CN were much more efficient in generating Mn^V -oxo than reactions in CH_2Cl_2 or $PhCF_3$. In CH_3CN solutions, the efficiency of formation of Mn^V -oxo species was **2** > **4** \approx **6**.

Catalytic Competitive Oxidations. A solution containing equal amounts of two substrates, e.g., *cis*-stilbene (0.5 mmol) and diphenylmethane (0.5 mmol), manganese(III) porphyrin catalyst (1 μ mol), and an internal standard (benzyl acetate, 0.5 mmol) was prepared. *m*-CPBA or $PhIO$ (0.2 mmol) was added, and the solution was stirred under inert atmosphere for the desired time at ambient temperature (ca. 22 °C). The amounts of substrates before and after the reactions were determined by GC (FID, Carbowax or DB-5). The values reported in Table S2 are the average of 2 or 3 runs.

LFP study of Mn(TPFPP)(NO₃). Based on literature reports that the irradiation of the nitrate salts of manganese porphyrin complexes, such as Mn(TPP)(NO₃), would produce the manganese(IV)-oxo intermediate, a similar LFP study of Mn(TFPPP)(NO₃) was also conducted. As shown in Figure S1, a transient species with a weak absorption band at 425 nm was immediately formed. In the presence of a reactive substrate such as *cis*-stilbene, the rate constant for decay at 425 nm ($k_0 = 170 \text{ s}^{-1}$) did not change. We assign the species with λ_{max} at 425 nm as the Mn^{IV}-oxo porphyrin intermediate.

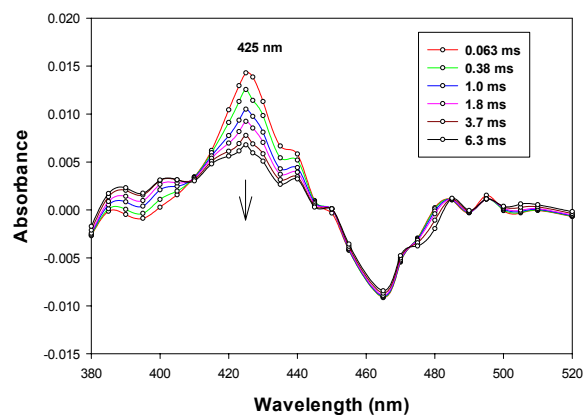


Figure S1. Time-resolved spectrum following LFP of Mn(TPFPP)(NO₃) in acetonitrile.

Table S1. Rate Constants for Decay of Manganese(V)-Oxo Intermediates in the presence of Various Substrates

| Substrate (Mn ^V =O) species | Concentration (M) | k_1/s^{-1} | k_2/s^{-1} |
|---|-------------------|--------------|--------------|
| <i>cis</i> -stilbene (2) | 0 | 1400 | 218 |
| | 0.001 | 2030 | 211 |
| | 0.002 | 2870 | 256 |
| | 0.003 | 3200 | 243 |
| | 0.004 | 3780 | 223 |
| | 0.005 | 4300 | 257 |
| | 0.006 | 5200 | 285 |
| diphenylmethane (2) | 0.001 | 1530 | 214 |
| | 0.003 | 2100 | 219 |
| | 0.006 | 2660 | 225 |
| | 0.01 | 3030 | 216 |
| | 0.015 | 3420 | 222 |
| PhEt- <i>d</i> ₀ (2) | 0.0025 | 1780 | 169 |
| | 0.005 | 1970 | 142 |
| | 0.0075 | 2380 | 174 |
| | 0.01 | 2700 | 197 |
| | 0.0125 | 2980 | 243 |
| | 0.015 | 3300 | 198 |
| PhEt- <i>d</i> ₁₀ (2) | 0.0025 | 1480 | 162 |
| | 0.005 | 1560 | 166 |
| | 0.0075 | 1640 | 142 |
| | 0.01 | 1800 | 162 |
| | 0.0125 | 2000 | 174 |
| | 0.015 | 2200 | 177 |
| <i>cis</i> -stilbene (4) | 0 | 150 | 30 |
| | 0.001 | 170 | 27 |
| | 0.005 | 230 | 26 |
| | 0.010 | 283 | 25 |
| | 0.015 | 343 | 26 |
| <i>cis</i> -stilbene (6) | 0 | 90 | 13 |
| | 0.001 | 150 | 14 |
| | 0.002 | 200 | 10 |
| | 0.003 | 235 | 15 |
| | 0.004 | 270 | 15 |
| | 0.005 | 310 | 20 |
| diphenylmethane (6) | 0.01 | 140 | 10 |
| | 0.015 | 185 | 15 |
| | 0.02 | 206 | 10 |
| | 0.03 | 265 | 15 |
| | 0.04 | 320 | 12 |
| | 0.05 | 377 | 10 |

Table S2. Competitive Oxidations Catalyzed by Mn^{III}(TPFPP)(Cl) using PhIO or *m*-CPBA as Terminal Oxidant

| | Entry | Oxidant | Solvent | Time (h) | k_{rel}^a | k_{rel}^b |
|--------------------------------------|----------------|----------------|--------------------|----------|--------------------|--------------------|
| | 1 | PhIO | CDCl ₃ | 20 | 4.7 | |
| <i>cis</i> -stilbene | 2 | PhIO | CH ₃ CN | 48 | 4.1 | 4.7 |
| + | 3 | <i>m</i> -CPBA | CDCl ₃ | 1 | 6.3 | |
| diphenylmethane | 4 | <i>m</i> -CPBA | CH ₃ CN | 1 | 5.6 | |
| | 5 ^c | <i>m</i> -CPBA | CH ₃ CN | 1 | 8.5 | 7.5 |
| ethylbenzene- <i>d</i> ₀ | 6 | PhIO | CH ₃ CN | 20 | 2.1 | 2.3 |
| + | 7 | <i>m</i> -CPBA | CH ₃ CN | 1 | 2.6 | |
| ethylbenzene- <i>d</i> ₁₀ | | | | | | |

^a Based on the conversions of substrates. ^b The ratios from LFP kinetic studies are listed for comparison. ^c Mn^{III}(TMPyP)(Cl) was used as catalyst instead of the Mn^{III}(TPFPP)(Cl).