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SUPPORTING INFORMATION

Title: Kinetics of (Porphyrin)manganese(III)-Catalyzed Olefin Epoxidation with a Soluble Iodosylbenzene Derivative
Author(s): James P. Collman,* Li Zeng, Hong J. H. Wang, Aiwen Lei, John I. Brauman
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5,10,15-Tris(pentafluorophenyl)-20-(3-nitrophenyl)porphyrin 5. Dipyrromethane **3**[41] (1.29 g, 4.1 mmol), dipyrromethane **4**[41] (1.0 g, 3.7 mmol), and pentafluorobenzaldehyde (1.53 g, 7.8 mmol) were dissolved in $CHCl_3$ (800 mL). N_2 was bubbled through the solution for 10 minutes. $BF_3.OEt_2$ (0.28 mL, 2.31 mmol) was then added and the reaction mixture was stirred at room temperature for 3.5 hours under N_2, followed by addition of triethylamine (3 mL). After DDQ (2.65 g, 11.7 mmol) was added, the reaction mixture was stirred for a further 3 hours. The mixture was concentrated and filtered through a silica pad eluting with hexane/CH_2Cl_2 (2:1). The porphyrin fractions were collected together. The mixture (three porphyrins) was separated using chromatography (silica, hexane/CH_2Cl_2, 1:4). The desired porphyrin **3** was obtained as the second fraction (yield: 150 mg, 4.3%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 8.77 (d, J = 4.8 Hz, 2H), 8.75 (d, J = 4.8 Hz, 2H), 8.71 (s, 1H), 8.63 (d, J = 4.8 Hz, 2H), 8.60 (d, J = 4.8 Hz, 2H), 8.22 (m, 1H), 7.78 (m, 1H), 7.05 (dd, J = 8.0 Hz, J = 8.0, 1H), -2.90 (b, 2H).

5,10,15-Tris(pentafluorophenyl)-20-(3-aminophenyl)porphyrin 6. Nitroporphyrin **5** (100 mg, 0.11 mmol) was mixed with $SnCl_2.2H_2O$ (75 mg, 0.33mmol) in concentrated HCl (20 mL). The mixture was stirred at room temperature under N_2 for 2 days. The reaction was then cooled with an ice bath and NH_4OH was added in portions with caution. After the acid was completely neutralized, the mixture was taken into CH_2Cl_2. The organic layer was washed with water thoroughly before evaporated to dryness. The crude product was purified on silica column eluting first with 1: 4 and then 1:1 CH_2Cl_2/hexanes. The desired aminoporphyrin **6** was collected as the second fraction (yield: 67 mg, 70%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 9.11 (d, J = 4.8 Hz, 2H), 8.73 (d, J = 4.8 Hz, 2H), 8.71 (d, J= 4.8 Hz, 2H), 8.58 (d, J = 4.8 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.38 (dd, J = 8.0 Hz, J = 7.6 1H), 7.11 (t, J = 2.0 Hz, 1H), 6.71 (m, 1H), 3.09 (s, 2H), -2.82 (b, 2H).

4-Prop-2-ynyloxy-benzoic acid methyl ester 7. Methyl-4-hydroxybenzoate (1.52g, 10 mmol) and propargyl bormide (80% wt. Solution in toluene, 2.23g, 15 mmol) were dissolved in acetone (75 mL). Finely powdered potassium carbonate (2.76g, 20 mmol) was added to the solution and the reaction mixture was stirred overnight at room temperature. The solvents were evaporated after the reaction was completed, and water (100 mL) was added to the residue. The aqueous phase was extracted with ethyl acetate (3 × 100 mL) and the organic phases were combined, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography (silica, 5% ethyl acetate in dichloromethane) to afford the product as an off-white powder (1.82g, 96%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.99 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 4.72 (d, J = 2.0 Hz, 2H), 3.87 (s, 3H), 2.53 (d, J = 2.0Hz, 1H).

4-Prop-2-ynyloxy-benzoic acid 8. To a solution of 4-prop-2-ynyloxy-benzoic acid methyl ester (0.95g, 5.0 mmol) in methanol (50 mL) was added sodium hydroxide (1.0g, 25 mmol) in portions. Water (5 mL) was subsequently added to increase the solubility of NaOH. The reaction mixture was stirred overnight at room temperature. Diluted H_2SO_4 (2M) was added to the reaction mixture until the pH of the aqueous phase was <1. The aqueous phase was then extracted with ethyl acetate (3 × 100 mL). The organic layers were combined, washed with water (100 mL), dried over Na_2SO_4, and evaporated to dryness to afford the acid (0.87g, 99%). ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): δ = 12.6 (br, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 4.90 (d, J = 2.0 Hz, 2H), 2.49 (d, J = 2.0 Hz, 1H).

Porphyrin containing the alkyne tail 9. Acid **8** (17.6 mg, 0.10 mmol) was dissolved in dry MeCN (10 mL) under N_2. To this solution was added oxalyl chloride (0.1 mL) and the mixture was stirred for 5 hours at room temperature. The solvent and the excessive oxalyl chloride were removed under vacuum and the residue was dissolved in dry MeCN (5 mL). To the solution was added aminoporphyrin **6** (17 mg, 19 μmol) solution in CH_2Cl_2 (5 mL), and the mixture was stirred for 3 hours at room temperature. After the reaction was completed (monitored by TLC), normal workup and flash chromatography (CH_2Cl_2/MeOH 20:1) afforded 16 mg of the desired product (yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.04 (d, *J* = 5.2 Hz, 2H), 8.89-8.91 (m, 4H), 8.82-8.83 (m, 2H), 8.38 (t, *J* = 2.0 Hz, 1H), 8.18-8.21 (m, 1H), 8.10 (br, 1H), 7.98-8.00 (m, 1H), 7.87-7.89 (m, 2H), 7.75 (t, *J* = 7.6 Hz, 1H), 6.95-6.98 (m, 2H), 4.64 (d, *J* = 2.4 Hz, 2H), 2.50 (t, *J* = 2.4 Hz, 1H), -2.87 (s, 2H). HRMS calculated for $C_{54}H_{23}F_{15}N_5O_2$: 1058.1612; found: 1058.1600.

Manganese porphyrin 10: To a solution of porphyrin **9** (16 mg, 16 μmol) dissolved in DMF (2 mL) was added $Mn(OAc)_2{\cdot}4H_2O$ (20 mg, 80 μmol). The mixture was refluxed for 2 hr under air and the reaction was monitored by UV-vis. DMF was removed under vacuum after all the starting material was consumed. The residue was then dissolved in CH_2Cl_2 (20 mL) and the organic layer was then washed with H_2O (20 mL), saturated NH_4Cl aqueous solution (20 mL), and dried over Na_2SO_4. Flash chromatography (CH_2Cl_2/MeOH 5:1) afforded the manganese porphyrin in quantitative yield (17 mg).

ICP Analysis: *Preparation of high standard solution:* Mn standard solution (1 mg/1 mL in 2% aqueous HNO_3, 10 mL) and Cu standard solution (1 mg/1 mL in aqueous 2% HNO_3, 2 mL) were mixed in a volumetric flask. The mixture was diluted with distilled water to 500 mL.

Preparation of quality control (QC) solution: 3 mL of Mn standard solution (1 mg/1 mL in 2% aqueous HNO_3) and 0.5 mL of Cu standard solution (1 mg/1 ml in 2% aqueous HNO_3) were mixed in a volumetric flask and diluted with distilled water to 500 mL.

Sample preparation: 1. Acid method: in a typical test, a sample of silica-supported catalyst (10-20 mg, weighted accurately to at least 4 significant figures) of was suspended in concentrated HNO_3 (1 mL). The suspension was brought to boil for several minutes until the color of the suspension changed from light red to colorless. The suspension was cooled to room temperature and diluted to 10 mL in a volumetric flask with distilled water. The mixture was filtered and subjected to ICP analysis. 2. Base method: a sample of silica-supported catalyst (10-20 mg, weighted accurately to at least 4 significant figures) was weighted into a test tube, 2-3 drops of saturated KOH was added to the solid. The test tube was swirled to make sure all the silica support was broken down. The base was then neutralized with concentrated HNO_3. More acid was added and heat was required to obtain complete dissolution of the metal ions. The mixture was then diluted with distilled water to 10 mL. After filtration, the aqueous sample was subjected to ICP analysis.

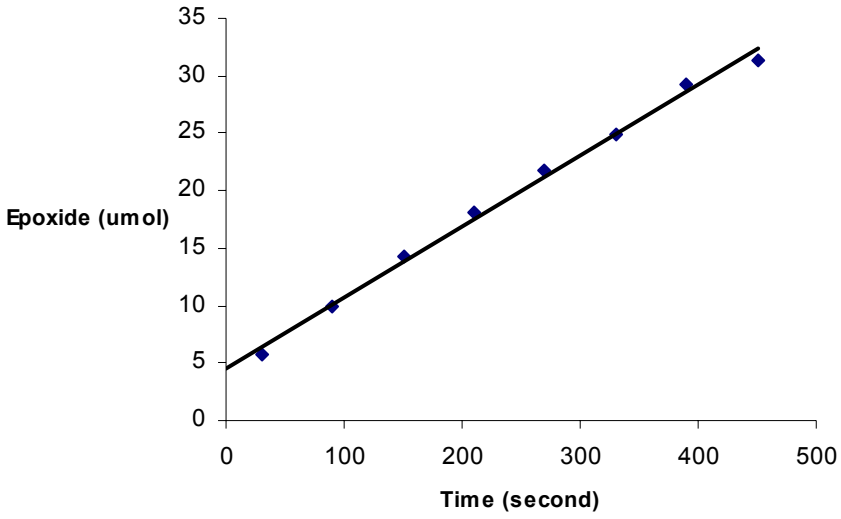

Figure S-1. Time course of *cis*-cyclooctene epoxidation.

Table S-1. Epoxidation of *cis*-cyclooctene at different substrate concentrations at 0°C.

	0.02M	0.08M	0.40M
yield[a]	81%	82%	84%
UV-VIS absorption[b]	0.69	0.70	0.71

a. Based on oxidant **1** (50 μmmol). *b*. 478nm.

Table S-2. Influence of additives on the epoxidation rate of *cis*-cyclooctene at 0°C.[a]

Additive	Additive Concentration (M)	Reaction Rate V (10^{-6}M/s)
none	--	2.53±0.07
cis-cyclooctene oxide	2×10^{-3}	2.50±0.07
styrene oxide	2×10^{-3}	2.55±0.10
ArI	0.01	2.50±0.05
phenylacetaldehyde	2×10^{-3}	2.45±0.07
benzyltriethylammonium chloride	1×10^{-3}	2.60±0.10

a. [*cis*-cyclooctene] = 0.08M; [**1**] = 0.01M; [**2**] = 1×10^{-5}M.

Table S-3. Epoxidation rates ($\times 10^{-6}$M/s) as a function of catalyst concentrations at 0°C.[a]

[**2**]	*cis*-cyclooctene	styrene	1-decene
2	0.47±0.03	0.73±0.03	--
5	1.23±0.03	1.70±0.03	0.46±0.03
10	2.53±0.07	3.30±0.07	0.92±0.03
20	5.07±0.13	6.43±0.13	1.80±0.10

a. [**1**] = 0.01M; [olefin] = 0.08 M.

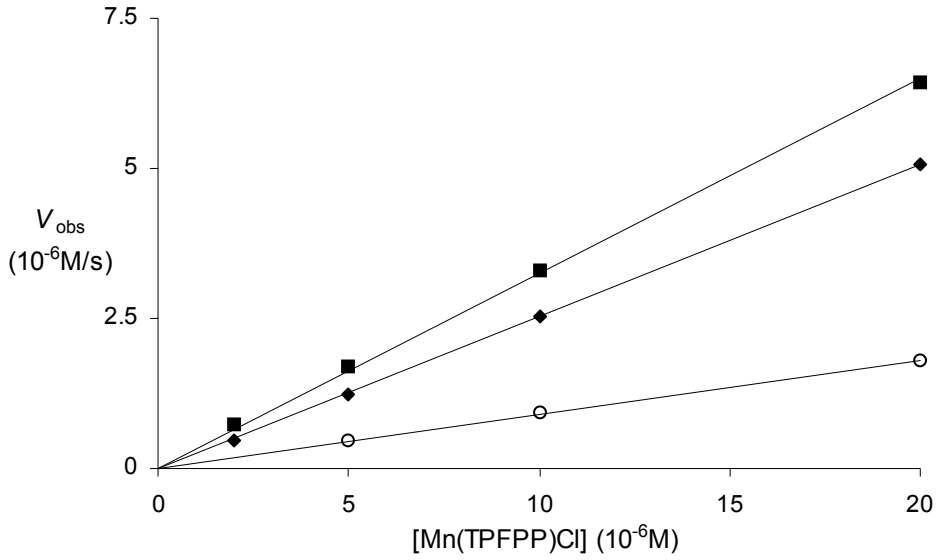

Figure S-2. Epoxidation rates as a function of catalyst concentrations (data from Table S-3). ♦: cis-cyclooctene; ■: styrene; ○: 1-decene.

Table S-4. Epoxidation rates ($\times 10^{-6}$M/s) as a function of oxidant concentrations at 0°C.[a]

[**1**]	*cis*-cyclooctene	styrene	1-decene
5×10^{-3}M	2.50±0.07	3.21±0.07	0.90±0.03
10×10^{-3}M	2.53±0.07	3.30±0.07	0.92±0.03
20×10^{-3}M	2.53±0.07	3.34±0.10	0.90±0.03

a. [**2**] = 1×10^{-5}M; [olefin] = 0.08 M.

Table S-5. Epoxidation rates as a function of substrate concentrations at 0°C ($\times 10^{-6}$M/s).[a]

[olefin]	*cis*-cyclooctene	styrene	1-decene
0.02M	1.93±0.07	2.00±0.07	0.55±0.07
0.04M	2.20±0.07	2.91±0.07	0.70±0.07
0.08M	2.53±0.07	3.30±0.07	0.92±0.03
0.16M	3.13±0.07	3.88±0.07	1.20±0.07
0.28M	--	4.43±0.07	1.27±0.07
0.32M	3.47±0.07	--	--
0.40M	3.53±0.07	4.73±0.07	1.40±0.07

a. [**1**] = 0.01M; [**2**] = 1×10^{-5}M.

Table S-6. Non-linear least-square fitting results for data in Table S-5.

	cis-cyclooctene	styrene	1-decene
Best-Fit Value			
V_{max} (10^{-6}M/s)	3.621	4.877	1.502
K_m (M)	0.02315	0.03077	0.04301
Standard Error			
V_{max} (10^{-6}M/s)	0.1484	0.1630	0.05118
K_m (M)	0.004521	0.004353	0.005489
95% Confidence Intervals			
V_{max} (10^{-6}M/s)	3.239-4.003	4.458-5.296	1.370-1.633
K_m (M)	0.0115-0.0347	0.0195-0.0419	0.0289-0.0571
Goodness of Fit			
Degree of Freedom	5	5	5
R^2	0.9810	0.9896	0.9914
Absolute Sum of Squares	0.1708	0.1652	0.01237
$S_{y,x}$	0.1849	0.1818	0.04973

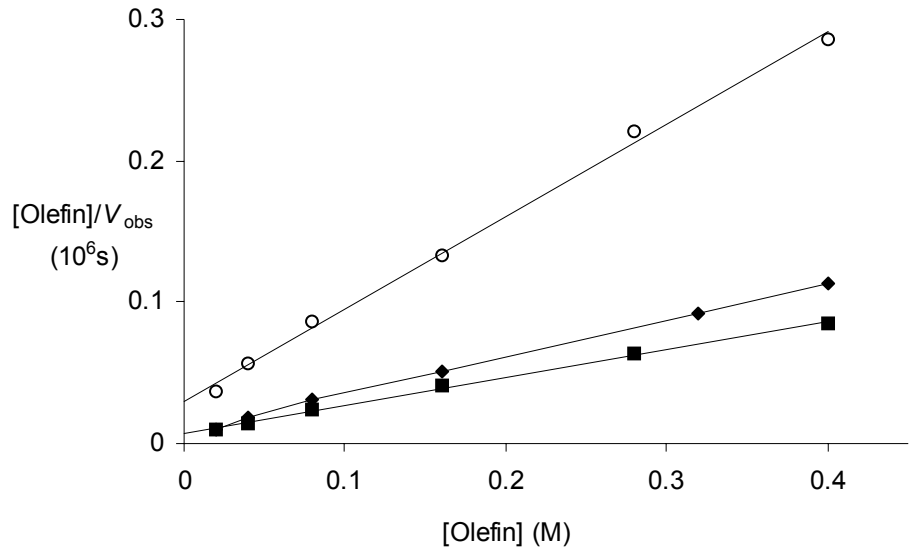

Figure S-3. Hanes Plot: plot of [Olefin]/V_{obs} against [Olefin] (data from Table S-4). ♦: cis-cyclooctene; ■: styrene; ○: 1-decene.

Since

$$V_{obs} = \frac{V_{max}[S]}{K_m + [S]} \qquad \text{(S-1)}$$

By taking the reciprocal of both sides of (S-1), we obtain (S-2).

$$\frac{1}{V_{obs}} = \frac{K_m}{V_{max}[S]} + \frac{1}{V_{max}} \qquad \text{(S-2)}$$

The plot of $1/V_{obs}$ against 1/[S], which is commonly known as Lineweaver-Burk or double-reciprocal plot, is not recommended without suitable weights.[42,43]

By multiplying both sides of (S-2) by [S], we get (S-3).

$$\frac{[S]}{V_{obs}} = \frac{[S]}{V_{max}} + \frac{K_m}{V_{max}} \qquad \text{(S-3)}$$

The plot of [S]/ V_{obs} against 1/[S], or Hanes plot, is recommended to display Michaelis-Menten kinetic data.[3] The intercept on Y-axis in Hanes plot is equal to K_m/V_{max}.

Table S-7. Epoxidation rates of *cis*-cyclooctene at difference temperatures ($\times 10^{-6}$M/s).[a]

[olefin]	20°C	10°C	0°C	-9°C
0.02M	6.94±0.03	4.26±0.07	1.93±0.07	0.92±0.03
0.04M	8.40±0.07	4.80±0.07	2.20±0.07	1.10±0.03
0.08M	10.14±0.07	5.60±0.07	2.53±0.07	1.10±0.03
0.16M	12.26±0.10	6.46±0.07	3.13±0.07	1.20±0.03
0.28M	--	--	--	--
0.32M	14.66±0.20	7.06±0.10	3.47±0.07	1.27±0.03
0.40M	--	--	3.53±0.07	--

a. [**1**] = 0.01M; [**2**] = 1×10^{-5}M.

Table S-8. Non-linear least-square fitting results for data in Table S-7.

	20°C	10°C	0°C	-9°C
Best-Fit Value				
V_{max} (10^{-6}M/s)	15.12	7.133	3.621	1.265
K_m (M)	0.03015	0.01644	0.02315	0.007429
Standard Error				
V_{max} (10^{-6}M/s)	0.8860	0.2757	0.1484	0.03406
K_m (M)	0.006635	0.003123	0.004521	0.001562
95% Confidence Intervals				
V_{max} (10^{-6}M/s)	12.66-17.58	6.368-7.898	3.239-4.003	1.156-1.373
K_m (M)	0.012-0.049	0.008-0.025	0.012- 0.035	0.003-0.012
Goodness of Fit				
Degree of Freedom	4	4	5	4
R^2	0.9806	0.9886	0.9810	0.9949
Absolute Sum of Squares	2.508	0.3608	0.1708	0.005625
$S_{y, x}$	0.7918	0.3003	0.1849	0.03750

Table S-9. Rates of Eyring studies (date from Tables S-7 and S-8).

T(°C)	k_2 (s^{-1})	1/T(K^{-1})	ln(k_2/T)
-9	0.127	0.003786	-7.640
0	0.362	0.003661	-6.626
10	0.713	0.003532	-5.984
20	1.512	0.003411	-5.267

Table S-10. Rates of epoxidation of *para*-substituted styrenes at 0°C ($\times 10^{-6}$M/s).[a]

[olefin]	4-OMe	4-Me	4-H	4-NO_2
0.02M	4.00±0.10	2.65±0.07	2.00±0.07	1.10±0.03
0.04M	5.00±0.10	3.37±0.10	2.91±0.07	--
0.08M	5.92±0.10	3.80±0.10	3.30±0.07	2.00±0.07
0.16M	6.66±0.13	4.22±0.10	3.88±0.07	2.10±0.07
0.28M	--	--	4.43±0.07	--
0.40M	7.28±0.17	4.83±0.10	4.73±0.07	2.66±0.07

a. [**1**] = 0.01M; [**2**] = 1×10^{-5}M.

Table S-11. Non-linear least-square fitting results for data in Table S-10.

	4-OMe	4-Me	4-H	4-NO_2
Best-Fit Value				
V_{max} (10^{-6}M/s)	7.488	4.842	4.877	2.740
K_m (M)	0.01890	0.01786	0.03077	0.03175
Standard Error				
V_{max} (10^{-6}M/s)	0.1195	0.1371	0.1630	0.1488
K_m (M)	0.001395	0.002401	0.004353	0.007369
95% Confidence Intervals				
V_{max} (10^{-6}M/s)	7.156-7.820	4.461-5.222	4.458-5.296	2.267-3.214
K_m (M)	0.015-0.023	0.011-0.024	0.019-0.042	0.008-0.055
Goodness of Fit				
Degree of Freedom	4	4	5	3
R^2	0.9981	0.9938	0.9896	0.9879
Absolute Sum of Squares	0.06680	0.09051	0.1652	0.05264
$S_{y, x}$	0.1292	0.1504	0.1818	0.1325

Table S-12. Rates of Hammett studies (data from Tables S-10 and S-11).

substituent	σ^+	$k_2(s^{-1})$	$\lg k_2$
4-OMe	-0.78	0.749	-0.1255
4-Me	-0.31	0.484	-0.3152
4-H	0.00	0.488	-0.3116
4-NO_2	0.79	0.274	-0.5622

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