

Reaction mechanism of the highly efficient catalytic decomposition of peroxyxynitrite by the amphipolar iron(III) corrole 1-Fe.

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Supporting Information

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1. Kinetic measurements:

k_{cat} values of the 1-Fe catalyzed decomposition of PN:

[1-Fe] M	k_{obs} (s ⁻¹)	rate (M ⁻¹ s ⁻¹)	R ²	error
2.5E-06	3.967	2.03E+06	0.9871	1.41E+05
5.0E-06	11.32			
7.5E-06	14.36			
1.0E-05	21.21			
1.3E-05	26.04			
1.5E-05	29.31			
0.0E+00	0.34			

Table S1. Observed rate constants for decomposition of peroxyxynitrite (385 μM , 0.15 M phosphate buffer, pH 7.4, 25 °C) as a function of the concentration of 1-Fe.

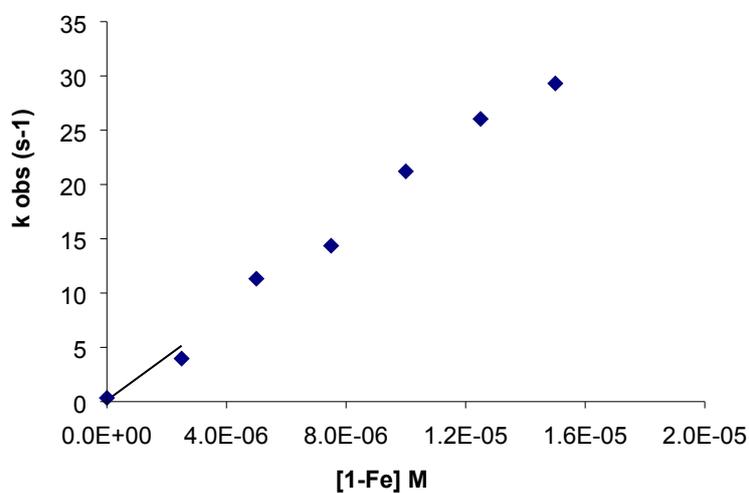


Figure S1. Plot of the observed rate constants for decomposition of peroxyxynitrite (385 μM , 0.15 M phosphate buffer, pH 7.4, 25 °C) as a function of the concentration of **1-Fe**.

Eyring plot (Fig. 1):

Temp. K	[1-Fe] M	k_{obs}	rate	R ²	error	1/T x 10 ³	lnk obs	ln(k/t)	error
310	2.50E-6	5.692	5.16E+6	0.9843	3.76E+5	3.2258	15.4555	9.7189	0.0729
	5.00E-6	17.19							
	7.50E-6	28.72							
	1.00E-5	39.41							
	1.25E-5	59.03							
304	2.50E-6	5.939	3.38E+6	0.9919	1.53E+5	3.2895	15.0334	9.3164	0.0453
	5.00E-6	16.98							
	7.50E-6	24.23							
	1.00E-5	35.16							
	1.25E-5	40.38							
298	2.50E-6	3.967	2.03E+6	0.9871	1.41E+5	3.3557	14.5087	8.8116	0.0704
	5.00E-6	11.32							
	7.50E-6	14.36							
	1.00E-5	21.21							
	1.25E-5	26.04							
288	2.50E-6	3.131	1.25E+6	0.9762	9.78E+4	3.4722	14.0387	8.3757	0.0782
	5.00E-6	7.276							
	7.50E-6	10.53							
	1.00E-5	13.41							
	1.25E-5	17.69							
278	2.50E-6	0.7402	7.08E+5	0.9915	3.28E+4	3.5971	13.4698	7.8421	0.0463
	5.00E-6	3.179							
	7.50E-6	5.026							
	1.00E-5	6.619							
	1.25E-5	7.921							
	1.50E-5	9.961							

Table S2. Observed rate constants for decomposition of peroxyxynitrite (385 μ M, 0.15 M phosphate buffer, pH 7.4) as a function of the concentration of **1-Fe**.

The effect of ascorbate on the non-catalyzed and 1-Fe catalyzed decomposition of PN (Fig. 5):

[ascorbate] μM	[1-Fe] M	k _{obs} (s ⁻¹)	k _{cat} (M ⁻¹ s ⁻¹)	R ²	error
0	2.50E-06	1.69	1.56E+06x - 2.304	0.9991	2.72E+04
	5.00E-06	5.315			
	7.50E-06	9.43			
	1.00E-05	13.6			
	1.25E-05	17.1			
400	2.50E-06	20.55	6.63E+06x + 5.415	0.9915	3.55E+05
	5.00E-06	38.02			
	7.50E-06	59.46			
	1.00E-05	70.55			
	1.25E-05	87.18			
1000	5.00E-06	62.5	9.62E+07x+11.663	0.9902	6.76E+05
	7.50E-06	81.05			
	1.00E-05	105.37			
	1.25E-05	134.6			

Table S3. Observed rate constants for decomposition of peroxynitrite (385 μM, 0.15 M phosphate buffer, pH 7.4, 25 °C) as a function of the concentration of **1-Fe** with 0, 400 or 1000 μM ascorbate.

2. Fluorescein nitration experiments:

Influence of peroxyxynitrite concentration on the yield of fluorescein nitration (Fig. 6):

	[PN] μ M	Area carboxyfluorescein	Area Fluorescein	Area nitrofluorescein	%nitro
no cat	100	8749008	5559760.62	773317.886	8.84
	200	7181910	5064414.66	1294479.78	18.02
	400	6816112	3423481.56	2521530.37	36.99
	600	6532926	2430013.74	3379061.31	51.72
	800	6935329	1997458.98	4305399.67	62.08
	1000	6482432	1627612.2	4267354.85	65.83
1-Fe	100	8599268	4935095.34	1570074.44	18.26
	200	10364334	4118077.86	4835288.06	46.65
	400	9517411	1860760.44	6980809.09	73.35
	600	9445846	1378727.4	7542888.72	79.85
	800	9118524	1055327.64	7682493.57	84.25
	1000	8758016	586332.78	7943327.39	90.70
1-Mn	200	7955917	8668670.58	52918.624	0.67
	400	7800880	8391335.94	179608.396	2.30
	600	8029129	8331814.26	241809.678	3.01
	800	7793879	7871066.16	385146.014	4.94
	1000	7360348	7166397.96	403978.982	5.49

Table S4. % Nitrofluoresceine with increasing concentration of peroxyxynitrite. Reaction conditions: 1 μ M catalyst (1-Fe or 1-Mn), 100 μ M fluorescein in 0.2 M phosphate buffer at pH=7.4.

Effect of ascorbate on the nitration yield of fluorescein (Fig. 7):

no cat				
[ascorbate] μM	Area carboxyfluorescein	Area fluorescein	Area nitrofluorescein	% nitro
0	7856586	2916716.22	4173400.308	53.12
250	7262008	6209776.08	990381.92	13.64
500	7311816	6824460.66	0	0.00
1000	7684401	7498548.36	0	0.00

1-Fe				
[ascorbate] μM	Area carboxyfluorescein	Area fluorescein	Area nitrofluorescein	% nitro
0	7947274	125708.94	7508307.73	94.48
250	8240689	3898267.62	4298080.952	52.16
500	7485758	6513475.5	1051039.858	14.04
1000	7463588	7557152.34	136721.508	1.83

Table S5. % Nitrofluorescein with different concentrations of ascorbate. Reaction conditions: 1 μM **1-Fe**, 100 μM fluorescein, 1000 μM peroxyxynitrite in 0.2 M phosphate buffer at pH=7.4.

Effect of various catalysts on the nitration yield of fluorescein by peroxyxynitrite in solutions without and with ascorbate (Fig. 8):

	ascorbate μM	Area carboxyfluorescein	Area fluorescein	Are nitrofluorescein	% nitro
no cat	0	8097052	3603941.28	4318966.5	53.3
	250	8041416	4376302.68	1880081.5	23.38
1-Mn	0	7272660	6350798.64	665447.178	9.15
	250	7643381	7122519.36	419622.72	5.49
1-Fe	0	8117492	2595799.38	6443866.15	79.385
	250	7889365	3330376.62	4007007.66	50.79
1-Ga	0	7743235	4271838.78	2620309.6	33.84
	250	8101925	5002452.24	2243420.83	27.69
Fe-pOMe	0	7994016	2472221.1	4340750.59	54.3
	250	7465488	2819874.36	3596123.61	48.17
Mn-pOMe	0	7970952	7226778.06	470287.158	5.9
	250	8085018	7809421.8	201316.016	2.49
FeTSP	0	7312658	86144.1	7195653.7	98.4
	250	7283599	100136.46	7150309.28	98.17
MnTMpyP	0	8807148	701526.36	6489778.9	73.69
	250	8766241	1375470.42	5937496.38	67.73

Table S6. % Nitrofluorescein in solution with different catalysts (1 μM) on the nitration yield of fluorescein (100 μM) by peroxyxynitrite (1000 μM) in solutions without or with ascorbate (250 μM), in 0.2 M phosphate buffer, pH=7.4.