Supplementary Data

Kinetic Study of Nickel-Thiolate Oxygenation by Hydrogen Peroxide. Implications for Nickel-Containing Superoxide Dismutase.

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Experimental Procedures

Materials and Methods

All chemicals obtained from commercial sources were reagent-grade and used as received. The complex [*N*-{2-[(2-mercapto-2-methylpropyl)amino]ethyl}-1-methylimidazole-2-carboxamido]nickel(II) (**1**) was prepared by previously reported methods.[1] UV-visible data were collected using an Agilent 8453 spectrometer equipped with a variable temperature cell holder supplied by a Polyscience temperature regulator, model 1190A.

(1) Mullins, C. S.; Grapperhaus, C. A.; Frye, B. C.; Wood, L. H.; Hay, A. J.; Buchanan, R. M.; Mashuta, M. S. *Inorg. Chem.* **2009**, *48*, 9974.

Oxidation of 1

Stock solutions were prepared by dissolution of **1** (41.4 mg, 0.100 mmol) in 100 mL of .2 M phosphate buffers with pH values of 6.0, 7.0 and 8.0. Hydrogen peroxide solutions (0.0618, 0.124, 0.186, and 0.247 M) were prepared daily by serial dilution of a freshly prepared stock solution made from H_2O_2·urea (600 mg, 6.38 mmol) and deionized H_2O (10.00 mL). For each reaction, 1.00 mL of the stock solution of **1** was diluted with 1.00 mL deionized H_2O in a 1.0 cm cuvette, which was placed in the variable temperature cell holder. After the temperature equilibrated, 200 μL of a diluted H_2O_2 solution was injected. The reaction progress was monitored by the decrease in peak intensity at λ_{max} = 387 nm for 800 seconds in 1 s intervals. At least four trials were conducted for each reaction condition.

Evaluation of k_{obs}

Kinetic data for each trial was fit using SigmaPlot 8.0 according to equation 1 where At is the absorption at time *t*, $A_{baseline}$ is a constant value to correct for fluctuation in the baseline between samples, A_0 is the initial absorption value, *k* is k_{obs}, and t is time (in seconds).

$$A_t = A_{baseline} + A_0e^{-kt} \qquad (1)$$

Table S1. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 6.0 buffered aqueous solution at 303 K.[a]

$[H_2O_2]$ (M)	k_{obs} (s^{-1})	std. dev.
0.00580	0.003233	0.000007
0.00580	0.002877	0.000007
0.00580	0.002938	0.000010
0.0116	0.005651	0.000010
0.0116	0.005588	0.000011
0.0116	0.005411	0.000012
0.0116	0.004399	0.000010
0.0116	0.004991	0.000009
0.0174	0.007967	0.000014
0.0174	0.008169	0.000022
0.0174	0.008538	0.000019
0.0174	0.008704	0.000022
0.0232	0.011110	0.000027
0.0232	0.010200	0.000023
0.0232	0.009386	0.000028
0.0232	0.011760	0.000036
0.0232	0.013320	0.000052

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S2. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 7.0 buffered aqueous solution at 303 K.[a]

$[H_2O_2]$ (M)	k_{obs} (s^{-1})	std. dev.
0.00580	0.002663	0.000008
0.00580	0.002795	0.000008
0.00580	0.002732	0.000007
0.00580	0.003063	0.000008
0.0116	0.004858	0.000014
0.0116	0.005041	0.000011
0.0116	0.004861	0.000011
0.0116	0.005071	0.000017
0.0174	0.007661	0.000019
0.0174	0.007686	0.000021
0.0174	0.007535	0.000021
0.0174	0.008330	0.000033
0.0232	0.010580	0.000038
0.0232	0.011490	0.000075
0.0232	0.009940	0.000045
0.0232	0.010490	0.000049

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S3. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 8.0 buffered aqueous solution at 303 K.[a]

$[H_2O_2]$ (M)	k_{obs} (s^{-1})	std. dev.
0.00580	0.003123	0.000012
0.00580	0.003694	0.000012
0.00580	0.003668	0.000013
0.0058	0.003061	0.000011
0.0116	0.007031	0.000026
0.0116	0.007045	0.000025
0.0116	0.006424	0.000020
0.0116	0.006840	0.000020
0.0174	0.010270	0.000051
0.0174	0.010160	0.000044
0.0174	0.007649	0.000028
0.0174	0.010400	0.000060
0.0232	0.012390	0.000060
0.0232	0.012740	0.000087
0.0232	0.011670	0.000041
0.0232	0.009821	0.000026

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S4. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 6.0 buffered aqueous solution at 313 K.[a]

[H_2O_2] (M)	**k_{obs} (s^{-1})**	**std. dev.**
0.005624	0.005669	0.000012
0.005624	0.005880	0.000016
0.005624	0.005314	0.000010
0.005624	0.004884	0.000014
0.011249	0.010930	0.000028
0.011249	0.010460	0.000021
0.011249	0.010180	0.000035
0.016873	0.016930	0.000042
0.016873	0.014680	0.000026
0.016873	0.015270	0.000033
0.016873	0.017910	0.000073
0.016873	0.015800	0.000044
0.016873	0.017070	0.000070
0.022498	0.020710	0.000066
0.022498	0.023180	0.000137
0.022498	0.024260	0.000136
0.022498	0.022170	0.000134
0.022498	0.023080	0.000101

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S5. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 7.0 buffered aqueous solution at 303 K.[a]

$[H_2O_2]$ (M)	**k_{obs} (s^{-1})**	**std. dev.**
0.005624	0.005892	0.000014
0.005624	0.006668	0.000021
0.005624	0.005270	0.000018
0.005624	0.006450	0.000012
0.005624	0.005550	0.000013
0.011249	0.010400	0.000096
0.011249	0.010690	0.000106
0.011249	0.011230	0.000113
0.011249	0.012090	0.000103
0.016873	0.017690	0.000241
0.016873	0.019510	0.000211
0.016873	0.017590	0.000234
0.016873	0.017350	0.000126
0.016873	0.017040	0.000174
0.022498	0.020960	0.000230
0.022498	0.030720	0.000310
0.022498	0.025730	0.000332
0.022498	0.023150	0.000211
0.022498	0.026190	0.000380
0.022498	0.026290	0.000220

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S6. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 8.0 buffered aqueous solution at 313 K.[a]

[H_2O_2] (M)	**k_{obs} (s^{-1})**	**std. dev.**
0.005624	0.004835	0.000024
0.005624	0.004872	0.000022
0.005624	0.004845	0.000024
0.005624	0.004633	0.000029
0.011249	0.009674	0.000060
0.011249	0.011580	0.000134
0.011249	0.010560	0.000076
0.011249	0.010060	0.000076
0.016873	0.015260	0.000132
0.016873	0.016090	0.000138
0.016873	0.014260	0.000115
0.016873	0.015760	0.000132
0.022498	0.017840	0.000191
0.022498	0.019000	0.000141
0.022498	0.020050	0.000235
0.022498	0.021110	0.000207
0.022498	0.021430	0.000207

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S7. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 6.0 buffered aqueous solution at 323 K.[a]

$[H_2O_2]$ (M)	k_{obs} (s^{-1})	std. dev.
0.005624	0.008543	0.000032
0.005624	0.009209	0.000049
0.005624	0.009580	0.000056
0.005624	0.008556	0.000059
0.011249	0.022560	0.000163
0.011249	0.022020	0.000169
0.011249	0.021730	0.000184
0.011249	0.025290	0.000318
0.016873	0.032150	0.000333
0.016873	0.034420	0.000367
0.016873	0.031920	0.000310
0.016873	0.034460	0.000320
0.022498	0.049040	0.000978
0.022498	0.043210	0.000384
0.022498	0.039320	0.000371
0.022498	0.049210	0.000515

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S8. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 8.0 buffered aqueous solution at 303 K.[a]

$[H_2O_2]$ (M)	**k_{obs} (s^{-1})**	**std. dev.**
0.005624	0.018800	0.000118
0.005624	0.013370	0.000025
0.005624	0.012970	0.000036
0.005624	0.014390	0.000034
0.005624	0.014290	0.000062
0.011249	0.030260	0.000359
0.011249	0.029800	0.000093
0.011249	0.025250	0.000043
0.011249	0.029080	0.000299
0.016873	0.038890	0.000201
0.016873	0.039880	0.000171
0.016873	0.040340	0.000250
0.016873	0.039790	0.000212
0.022498	0.054570	0.000302
0.022498	0.052850	0.000257
0.022498	0.038740	0.000201
0.022498	0.050680	0.000345

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

Table S9. Observed rate constants for the direct oxidation of **1** by H_2O_2 in pH = 8.0 buffered aqueous solution at 303 K.[a]

$[H_2O_2]$ (M)	**k_{obs} (s^{-1})**	**std. dev.**
0.005624	0.008862	0.000054
0.005624	0.010410	0.000097
0.005624	0.009416	0.000092
0.005624	0.011230	0.000046
0.005624	0.009150	0.000068
0.005624	0.007785	0.000048
0.005624	0.009109	0.000056
0.011249	0.023480	0.000150
0.011249	0.017950	0.000047
0.011249	0.025360	0.000198
0.011249	0.024790	0.000197
0.016873	0.043530	0.000401
0.016873	0.036270	0.000207
0.016873	0.040330	0.000231
0.016873	0.033840	0.000152
0.022498	0.040230	0.000820
0.022498	0.052700	0.000588
0.022498	0.051650	0.000496
0.022498	0.049670	0.000472

[a] Conditions: [**1**] = 0.455 mM in 0.091 M phosphate buffer. Reactions were monitored at 387 nm. Reported *k* values determined by best fit of experimental data as described in the experimental section.

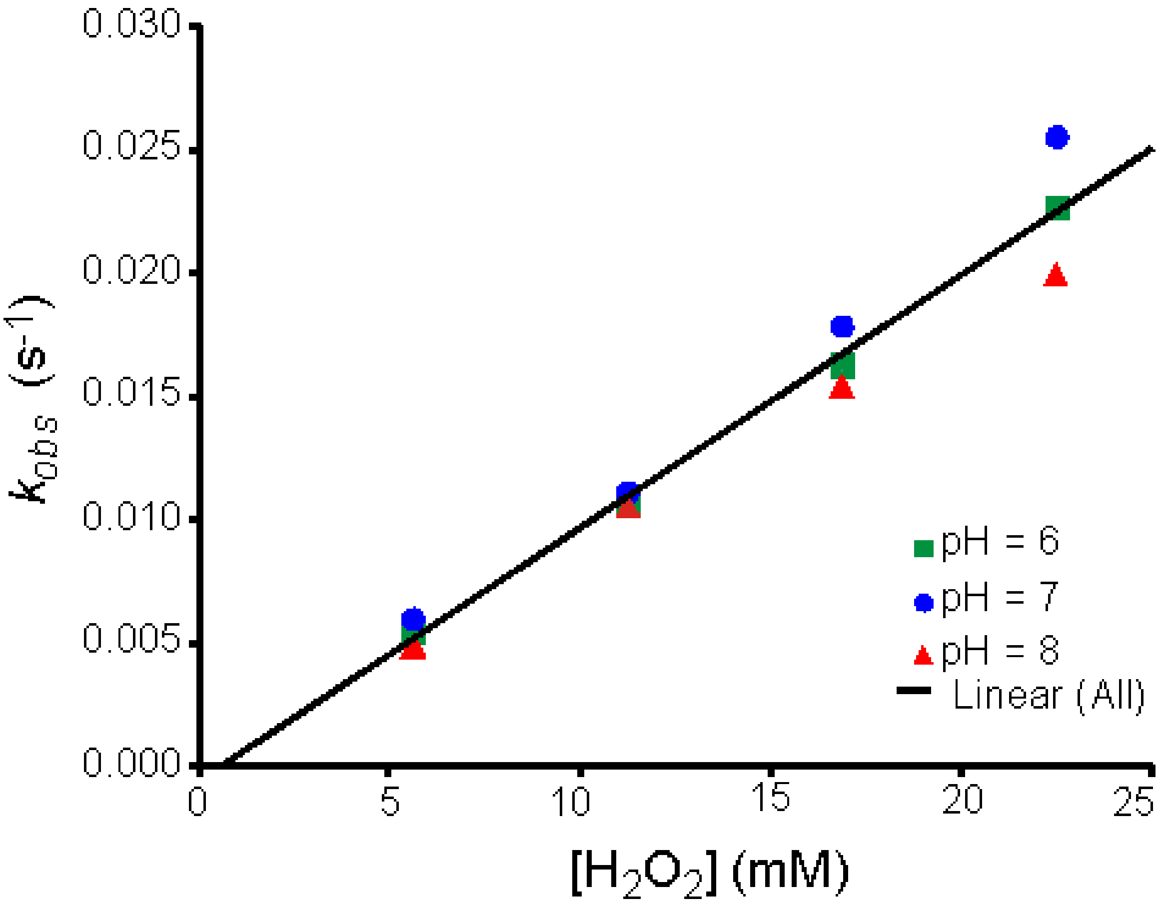

Figure S1. Plot of average k_{obs} x 10^2 (s^{-1}) versus [H_2O_2] (mM) for **1** at pH = 6.0, 7.0, and 8.0 at 313 K. Data from Table 1 of main text. The solid line represents the pH-independent fit of the data as determined by linear regression of the experimental results over all pH values.

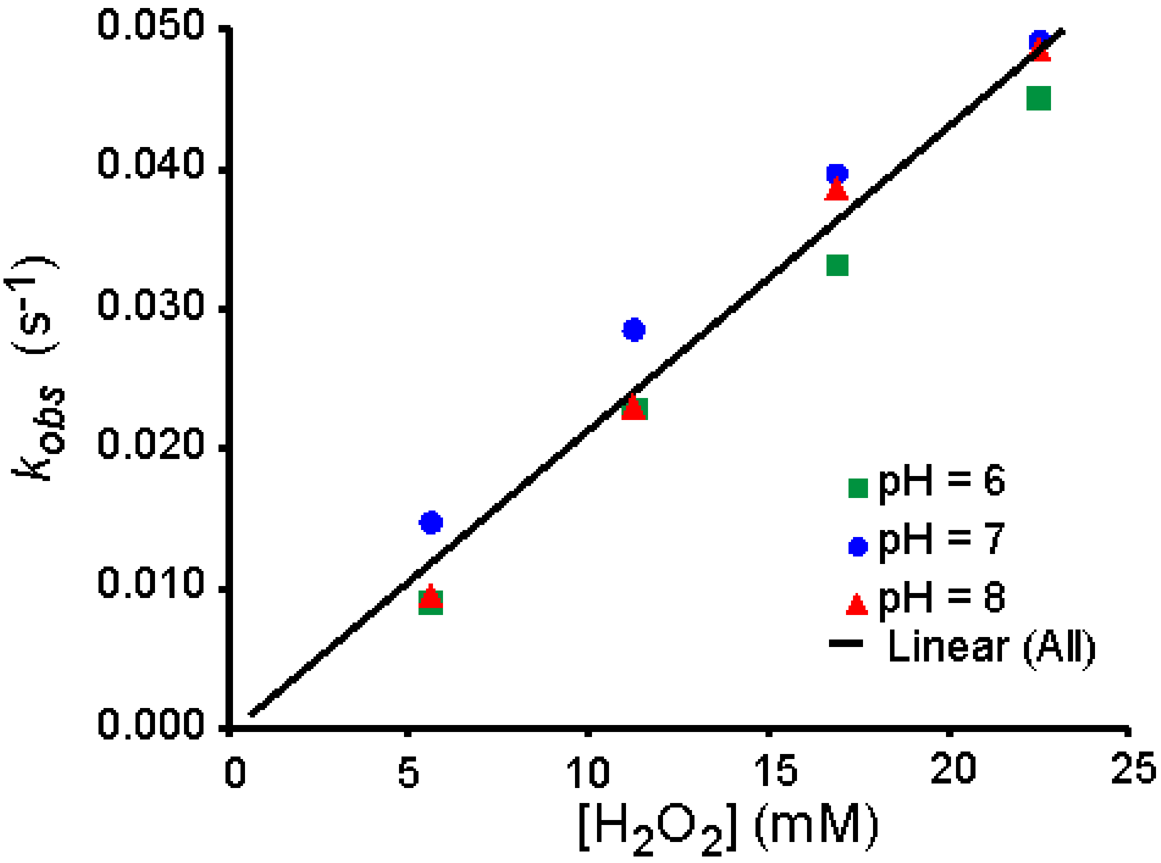

Figure S2. Plot of average k_{obs} x 10^2 (s^{-1}) versus [H_2O_2] (mM) for **1** at pH = 6.0, 7.0, and 8.0 at 323 K. Data from Table 1 of main text. The solid line represents the pH-independent fit of the data as determined by linear regression of the experimental results over all pH values.

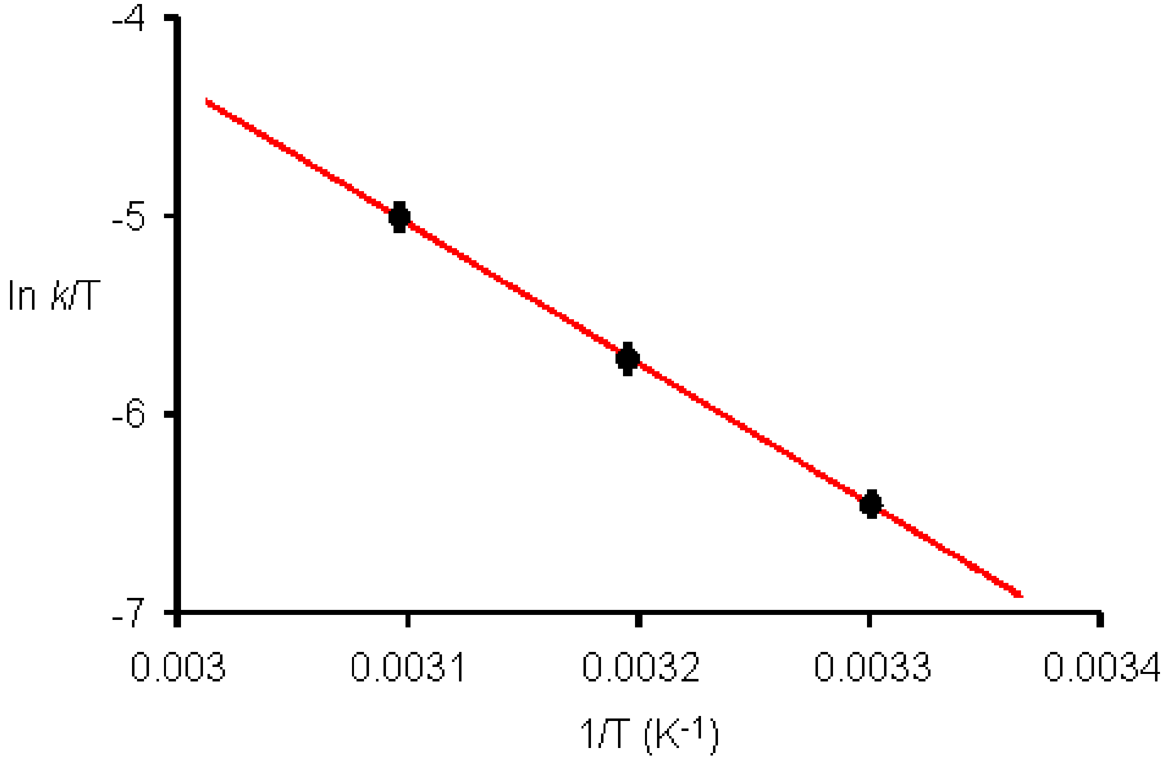

Figure S3. Eyring plot for the oxidation of **1** by H_2O_2.