Supporting Information

Kinetics and Mechanism of the Co(II)-assisted Oxidation of L-Ascorbic Acid by Dioxygen and Nitrite in Aqueous Solution

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Legends for Figures

**Figure S1**: Typical kinetic traces recorded for the reaction of complex I with L-ascorbic acid at 510 nm. Experimental conditions: [I] = 2 × 10^{-5} M, [H_2A]_T = 0.28 mM, 0.1 M acetate buffer (pH 5.8, solid line) and 0.1 M TRIS buffer (pH 7.0, dashed line) at 25 °C.

**Figure S2**: Plots of 1/k_{obs} vs. 1/[H_2A]_T as a function of temperature. Experimental conditions: [Co^{II}(L)(H_2O)_2]^{8-} = 2 x 10^{-5} M, [H_2A]_T = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 5.8).

**Figure S3**: Plot of k_{obs} vs. [H_2A]_T for the reduction of complex I by L-ascorbic acid under anaerobic conditions. Experimental conditions: [I] = 2 x 10^{-5} M, [H_2A]_T = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 3.8) at 25 °C.

**Figure S4**: Plot of lnK_4 versus 1/T for the reaction of complex I with ascorbate. Experimental conditions: [I] = 2 x 10^{-5} M, [H_2A]_T = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 5.8).

**Figure S5**: Eyring plot for reaction of complex I with L-ascorbic acid. Experimental conditions: [I] = 2 x 10^{-5} M, [H_2A]_T = (0.14 – 1.0) mM, 0.1 M acetate buffer (pH = 5.8).

**Figure S6**: Plot of lnk_{obs} vs. pressure for the reaction between complex I and L-ascorbic acid. Experimental conditions: [I] = 2 x 10^{-5} M, [H_2A]_T = 0.14 mM, 0.1 M MES buffer (pH = 5.8) at 25 °C.

**Figure S7**: Plot of lnK versus 1/T for the reaction of complex I with ascorbate. Experimental conditions: [I] = 2 x 10^{-5} M, [H_2A]_T = (0.14 – 1.0) mM, 0.1 M TRIS buffer (pH = 7.1).

**Figure S8**: Eyring plot for the reaction of complex I with ascorbate. Experimental conditions: [I] = 2 x 10^{-5} M, [H_2A]_T = (0.14 – 1.0) mM, 0.1 M TRIS buffer (pH = 7.1).
Figure S9: ESR spectrum of the product of the reaction between I and L-ascorbic acid under anaerobic conditions. Experimental conditions: [I] = 2.5 mM, [H₂A]₇ = 62.5 mM, 0.3 M TRIS buffer (pH = 7.4) at 85 K. The spectrum clearly shows the presence of Co II at 2660 G (see J. Krzystek, A. Ozarowski, J. Telser, Coord. Chem. Rev., 2006, 250, 2308) and L-ascorbic acid signals between 2750 and 3000 G (see J. T. Masiakowski and A. Lund, J. Chem. Soc., Faraday Trans., 1987, 83, 1869). The spectrum was recorded using the following parameters: number of scans = 4, center of field = 3000 G, sweep width = 2500 G, resolution = 8192 points, microwave frequency = 8.9 GHz, microwave power = 1 mW, modulation frequency = 100 kHz, modulation amplitude = 2 G, time constant = 100 ms, and sweep time = 120 s.

Figure S10: Dependence of the induction period on [H₂A]₇. Experimental conditions: [I]₇ = 2 x 10⁻⁵ M, [O₂] = 0.2 mM, [H₂A]₇ = (0.035 – 0.14) mM, 0.1 M TRIS buffer (pH = 7.0) at 25 °C.

Figure S11: Eyring plot for the oxidation of reduced complex I by O₂. Experimental conditions: [I]₇ = 2 x 10⁻⁵ M, [O₂] = 0.6 mM, [H₂A]₇ = 0.035 mM, 0.1 M TRIS buffer (pH = 7.0).

Figure S12: Plot of ln kobs₂ vs. pressure for the oxidation of the reduced form of complex I by O₂. Experimental conditions: [I]₇ = 2 x 10⁻⁵ M, [O₂] = 0.6 mM, [H₂A]₇ = 0.035 mM, 0.1 M TRIS buffer (pH = 7.0) at 35 °C.

Figure S13: Spectral changes observed during the oxidation of the reduced form of complex I by nitrite. Experimental conditions: [I]₇ = 2 x 10⁻⁵ M, [H₂A]₇ = 0.07 mM, [NaNO₂] = 100 mM, 0.1 M TRIS buffer (pH = 7.0) at 25 °C. Induction period omitted for clarity.

Figure S14: Eyring plot for the oxidation of the reduced form of complex I by NaNO₂. Experimental conditions: [I]₇ = 2 x 10⁻⁵ M, [H₂A]₇ = 0.14 mM, [NaNO₂] = 100 mM, 0.1 M TRIS buffer (pH = 7.0).

Figure S15: Plot of ln kobs₃ vs. pressure for the oxidation of the reduced form of complex I by NaNO₂. Experimental conditions: [I]₇ = 2 x 10⁻⁵ M, [H₂A]₇ = 0.14 mM, [NaNO₂] = 80 mM, 0.1 M TRIS buffer (pH = 7.0) at 35 °C.

Figure S16: ¹⁵N NMR spectrum recorded following the catalyzed oxidation of L-ascorbic acid by Na¹⁵NO₂. Experimental conditions: [I]₇ = 2 mM, [H₂A]₇ = 0.14 mM, [NaNO₂] = 2 M, 99% D₂O at 25 °C.
Figure S1
Figure S2
Figure S3

Data: Data1_B
Model: function
Equation: $y = \frac{kKx}{1 + Kx}$
Weighting:
y No weighting

$\chi^2$/DoF = 0.00019
$R^2 = 0.99659$

$k = 0.82328 \pm 0.01269$

$K = 9140.64763 \pm 660.41132$

$[H_2A]_r / \text{mM}$

$k_{obs} / \text{s}^{-1}$
Figure S4
Figure S5
Figure S6
Figure S7
Figure S8
Figure S9

- $g = 2.391, A = 188 \text{ G}$
- $g = 2.241, A = 39 \text{ G}$
- $g = 2.208, A = 47 \text{ G}$
Figure S10
Figure S11
Figure S12
Figure S13
Figure S14
Figure S15
Figure S16