Supplementary Information

Detailed Mechanism of the Autoxidation of N-hydroxyurea Catalyzed by a Superoxide Dismutase Mimic Mn(III) Porphyrin: Formation of the Nitrosylated Mn(II) Porphyrin as an Intermediate

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The UV-vis titrations and the data evaluation were carried out according to:
T. Weitner et. al. Dalton Trans., 2010, 39, 11568-11576

![Graphical representation of UV-vis titration results]

**Figure S1** UV-vis titration of Mn(III)TTEG (up) and Mn(II)TTEG (down) from pH 9.3 to pH 12.6. Left: spectral change, the pH increases with the arrows. Right: calculated individual spectrum of the protonated (black), the singly deprotonated (green) and the doubly deprotonated (red) species. c(Mn(III)TTEG) = 3.80 μM or c(Mn(II)TTEG) = 5.23 μM, I = 1.0 M, T = 25.0 °C, unaerobic conditions

The $^{17}$O-NMR measurements and the data evaluation were carried out according to:
A. Budimir et. al. Dalton Trans., 2010, 39, 4405–4410
**Figure S2** Reduced relaxation rates (circles: $1/T_{1r}$ and squares: $1/T_{2r}$ in s$^{-1}$ units) and chemical shift (triangles: $\Delta\omega_r$ in s$^{-1}$rad units) of Mn(III)TTEG studied as a function of temperature at pH 6. Lines: result of fit according to the reference above.

**Figure S3** The UV-vis titration of HU from pH 5.8 to pH 11.7, the pH increases with the arrow. $c(\text{HU}) = 1.00$ mM, $I = 1.0$ M, $T = 25.0$ °C, anaerobic conditions.
Figure S4. The effect of the conditions of illumination on the reaction of Mn(III)TTEG and HU. The green curve was recorded in a stopped-flow instrument with PMT detection, the white in a diode-array photometer and the red in a scanning photometer, under otherwise identical conditions. $c_0$(Mn(III)TTEG) = 7.50 μM, $c_0$(HU) = 15.0 μM, c(NaOH) = 5.0 mM, $c_0$(O$_2$) = 254 μM, I = 1.0 M, T = 25.0 °C.

Figure S5. Left: The UV-vis spectra of Mn(III)TTEG, Mn(II)TTEG and Mn(II)TTEG–NO. $c$(Mn(III)TTEG) = $c$(Mn(II)TTEG) =$c$(Mn(II)TTEG–NO) = 3.54 μM, c(NaOH) = 5.0 mM, anaerobic conditions. Right: The normalized UV-vis spectra of Mn(II)TTEG–NO and the intermediate of the reaction Mn(III)TTEG + HU recorded 150 s after mixing. $c_0$(Mn(III)TTEG) = 3.75 μM, $c_0$(HU) = 150 μM, c(NaOH) = 5.0 mM, $c_0$(O$_2$) = 254 μM, I = 1.0 M, T = 25.0 °C.
Figure S6 Measured (upper halves) and simulated (lower halves) isotopic distributions of species corresponding to Mn(III)TTEG (m/z 431.1882), Mn(II)TTEG (m/z 425.5203 and m/z 419.5167) and Mn(II)TTEG-NO (m/z 435.1818) as seen in Table 1.
Figure S7 The series of kinetic curves recorded during the concentration dependence measurements. Left: The initial concentration of HU was varied while that of Mn(III)TTEG was constant. \(c_0(\text{Mn(III)TTEG}) = 3.75 \mu \text{M}, \ c_0(\text{HU}) = \) from 0.763 \(\mu \text{M}\) to 114 \(\mu \text{M}\), \(c(\text{NaOH}) = 50 \text{mM}, \ c_0(\text{O}_2) = 254 \mu \text{M}, \ I = 1.0 \text{ M}, \ T = 25.0 ^\circ \text{C}\). Right: The initial concentration of Mn(III)TTEG was varied while that of HU was constant. \(c_0(\text{Mn(III)TTEG}) = \) from 1.25 \(\mu \text{M}\) to 6.25 \(\mu \text{M}\), \(c_0(\text{HU}) = 6.35 \mu \text{M}, \ c(\text{NaOH}) = 5.0 \text{mM}, \ c_0(\text{O}_2) = 254 \mu \text{M}, \ I = 1.0 \text{ M}, \ T = 25.0 ^\circ \text{C}\).

Figure S8 Left: The visible part of the spectrum of the 0.1 s old reaction mixture of Mn(III)TTEG + HU (green) compared to the spectrum of Mn(III)TTEG (red) recorded under identical conditions. \(c_0(\text{Mn(III)TTEG}) = 3.03 \mu \text{M}, \ c_0(\text{HU}) = 61.2 \mu \text{M}, \ c(\text{NaOH}) = 5.0 \text{mM}, \ c_0(\text{O}_2) = 254 \mu \text{M}, \ I = 1.0 \text{ M}, \ T = 25.0 ^\circ \text{C}\). Right: Dependence of the absorbance (0.10 s after mixing) at 430 nm on the initial HU concentration with constant initial Mn(III)TTEG concentration. The kinetic curves were recorded by stopped-flow PMT. \(c_0(\text{Mn(III)TTEG}) = 7.52 \mu \text{M}, \ c_0(\text{HU}) = \) from 1.56 \(\mu \text{M}\) to 78.1 \(\mu \text{M}\), \(c(\text{NaOH}) = 50 \text{mM}, \ c_0(\text{O}_2) = 254 \mu \text{M}, \ I = 1.0 \text{ M}, \ T = 25.0 ^\circ \text{C}\).
Figure S9 Left: Kinetic curves recorded with different initial concentrations of dissolved O₂. The initial concentrations of Mn(III)TTEG and HU were constant. Right: Dependence of the initial rate of reaction on the initial concentration of O₂. The dotted line indicates the solution saturated with air at atmospheric pressure. $c_0$(Mn(III)TTEG) = 4.98 μM, $c_0$(HU) = 101 μM $c$(NaOH) = 5.0 mM, $c_0$(O₂) = from 0.81 mg/L to 7.99 mg/L, I = 1.0 M, T = 25.0 °C.