Supporting information

Figure S1. Expanded view of the ESR simulations (**A'** and **B'**) of high resolution spectra from TCP• (**A**) and DCFP• (**B**). The experimental data are also presented in Figure **4A'** and Figure **4C'**. The DCFP• ESR signal has been "g-shifted" by 16 G in order to visually compare the hyperfine splittings. See text for simulation parameters.

Figure S2. IE-ESR spectra collected using immobilized myoglobin/H_2O_2 and immobilized dehaloperoxidase/H_2O_2 and TFP at pH 7.4. **A**, ESR spectrum of TFP• (collected using ~5 mg/ml enzyme), H_2O_2 (1 mM), TFP (1.0 mM), and 2.0 ml/min flow rate. ESR parameters: 9.74 GHz microwave frequency, 20 mW microwave power, 1 G_{pp} modulation amplitude, and an average of 10 - 84 sec scans with time constant of 328 ms. **B**, Time course showing formation of an inactive form of the DHP A known as compound RH; the ESR intensity was measured at 3475 G after each of the 10 scans. (see: Thompson, M. K., Franzen, S., Ghiladi, R. A., Reeder, B. J., and Svistunenko, D. A. (2010) Compound ES of Dehaloperoxidase Decays via Two Alternative Pathways Depending on the Conformation of the Distal Histidine. *J. Am. Chem. Soc., 132,* 17501-17510.)

Figure S1

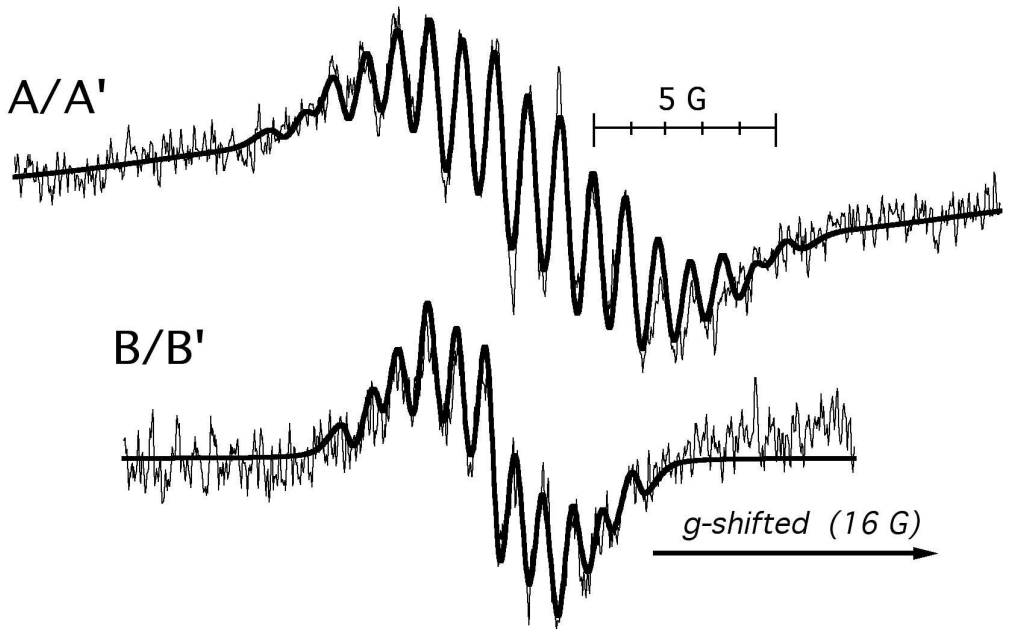
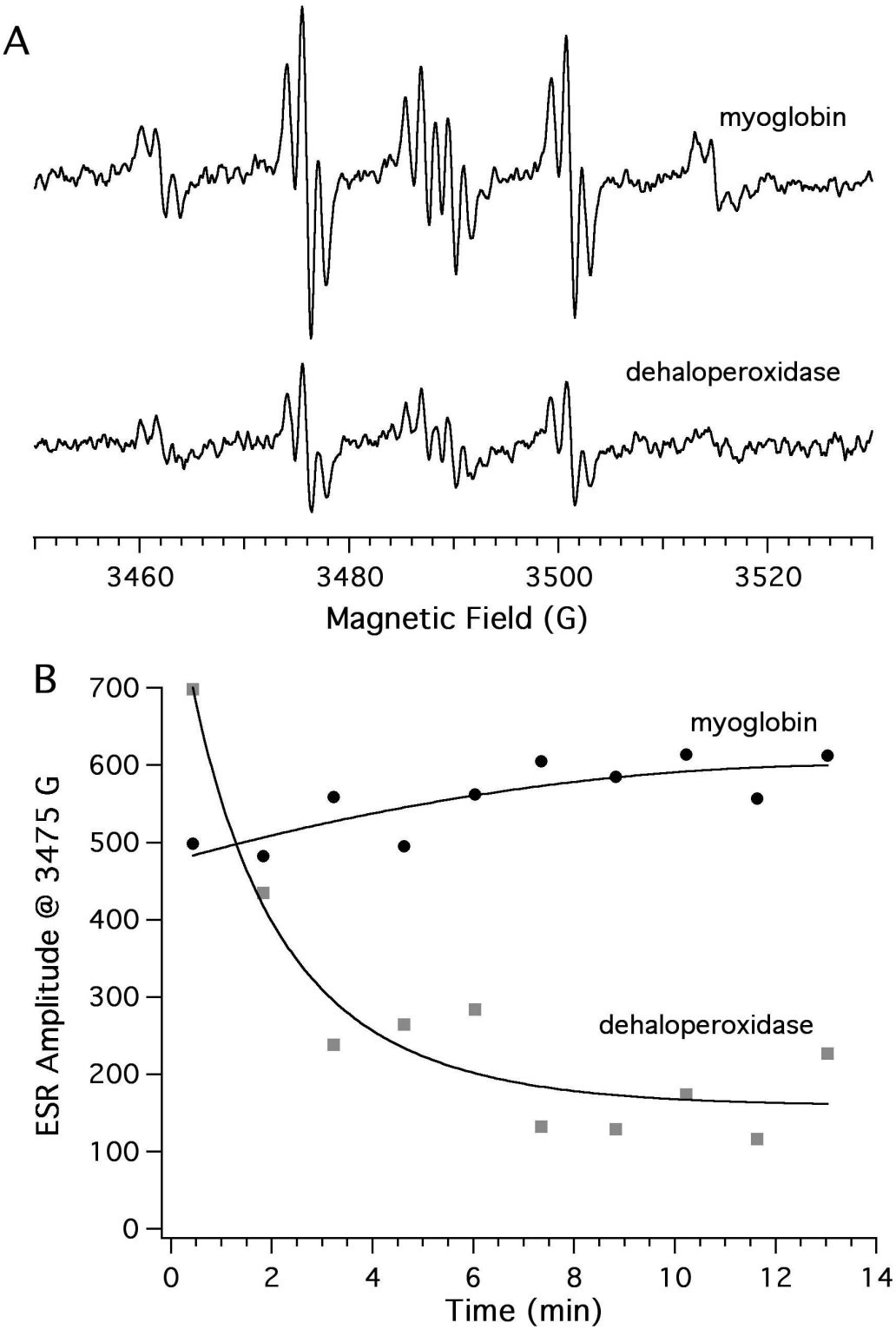


Figure 2S


A
myoglobin
dehaloperoxidase
3460
3480
3500
3520
Magnetic Field (G)
B
ESR Amplitude @ 3475 G
700
600
500
400
300
200
100
0
myoglobin
dehaloperoxidase
0
2
4
6
8
10
12
14
Time (min)