Supplemental Information

for

Observation of organometallic and radical intermediates formed during the reaction of methyl-coenzyme M reductase with bromoethanesulfonate

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Fig S1. Kinetics of MCR_{BES} radical decay determined by visible absorption spectral changes of MCR_{red1} upon addition of BES in presence of CoBSH.

Figure S2. 35 GHz EPR spectra at 2 K of MCR_{red1} in presence 1 mM CoB_6SH after addition of BES. The spectra are normalized to give the same signal intensity for $g_\perp$ of MCR_{ox1}. CW EPR spectra, recorded at 35.011 GHz, 1 G modulation amplitude, and two different microwave power settings: 20 dB (~1 mW; orange trace), 30 dB (~0.1 mW, red trace), are shown, along with echo-detected EPR spectra recorded at 34.851 GHz and two different repetition rates: 10 Hz (green trace), 50 Hz (blue trace); both used a Hahn spin echo sequence with: $\pi/2$ pulse width = 40 ns; delay time, τ = 600 ns. Signals from the three primary EPR-active species, MCR_{red1}, MCR_{ox1}, and MCR_{BES} radical are easily seen in the 35 GHz spectra. Also apparent is a weak signal from MCR_{red2}, with $g_\perp = 2.07$. A small signal from adventitious Mn(II) in the $g \sim 2.00$ region underlies the radical signal. EPR spectroscopy at 35 GHz and 2 K enhances Mn(II) signals; this one could be essentially invisible at X-band and 70 K.

Figure S3. Broad scan swept CW 35 GHz ^{1}H ENDOR spectra of MCR_{red1} recorded at 2 K at a field position on the MCR signal (g = 2.177, upper trace) and on the radical signal (g = 2.002, lower trace). As seen also in Figure 5 (which uses random hopping of rf), the MCR spectrum exhibits signal from a strongly coupled ^{1}H (*47*); in this case, both $\nu_\pm$ partners are observed. The radical signal exhibits much more severe baseline artifacts, however it is possible that there is ^{1}H hyperfine coupling of at least ~40 MHz, which would be consistent with the observation of hyperfine splitting by X-band EPR. Experimental conditions: microwave frequency, 35.010 GHz; modulation frequency, 2 G; microwave power, 20 dB (~100 μW); rf swept linearly from low to high frequency; 10 scans.

Fig S1. Kinetics of MCR_{BES} radical decay determined by visible absorption spectral changes of MCR_{red1} upon addition of BES in presence of CoBSH.

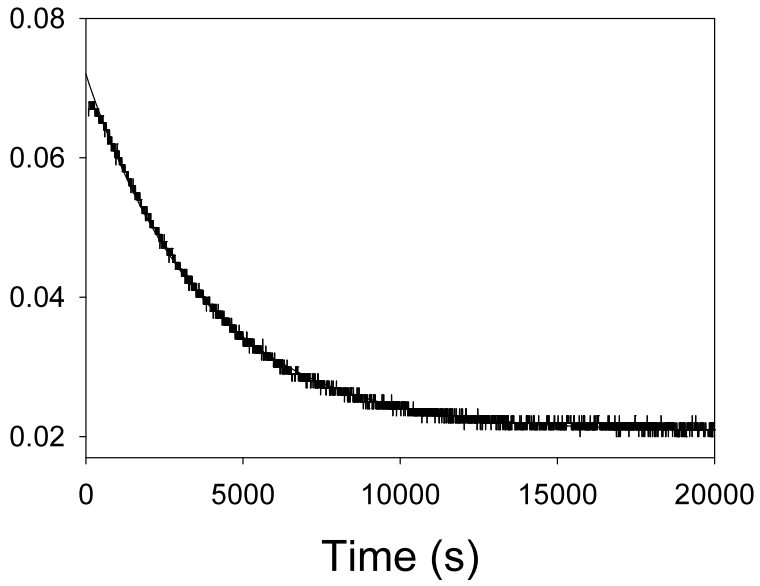
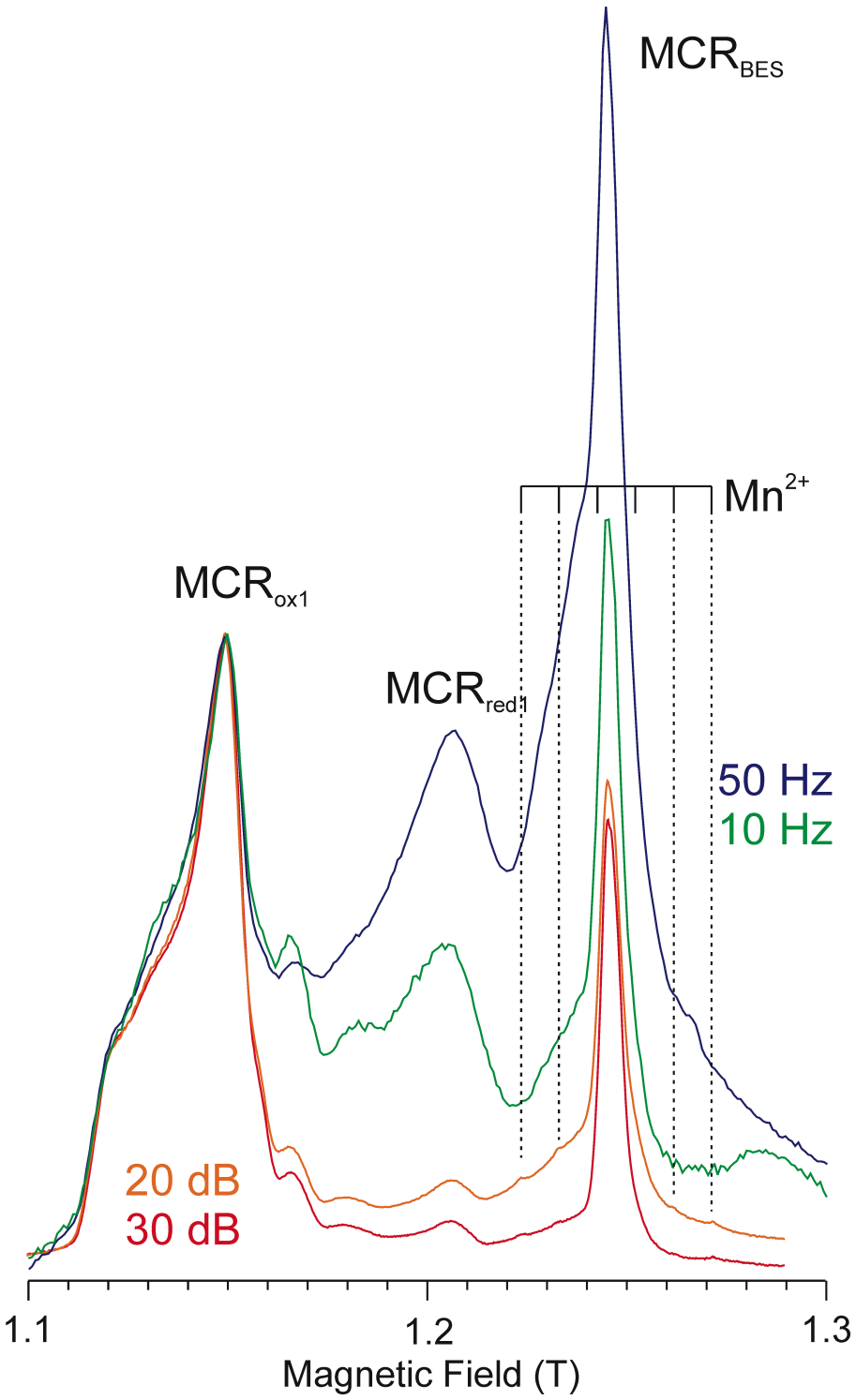


Figure S2. 35 GHz EPR spectra at 2 K of MCR_{red1} in presence 1 mM CoB_6SH after addition of BES.



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