Supporting information for:

Decay kinetics of sensitive bioinorganic species in a SuperFocus mixer at ambient conditions

Daniela Schurr[1], Florian Strassl[2], Patricia Liebhäuser[2], Günter Rinke[1], Roland Dittmeyer[1], Sonja Herres-Pawlis[2]

[1]Institut für Mikroverfahrenstechnik, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen
[2]Institut für Anorganische Chemie, Rheinisch-Westfälische Technische Hochschule Aachen, Landoltweg 1, 52074 Aachen, Germany

UV-Vis spectra of the stopped-flow at different temperatures

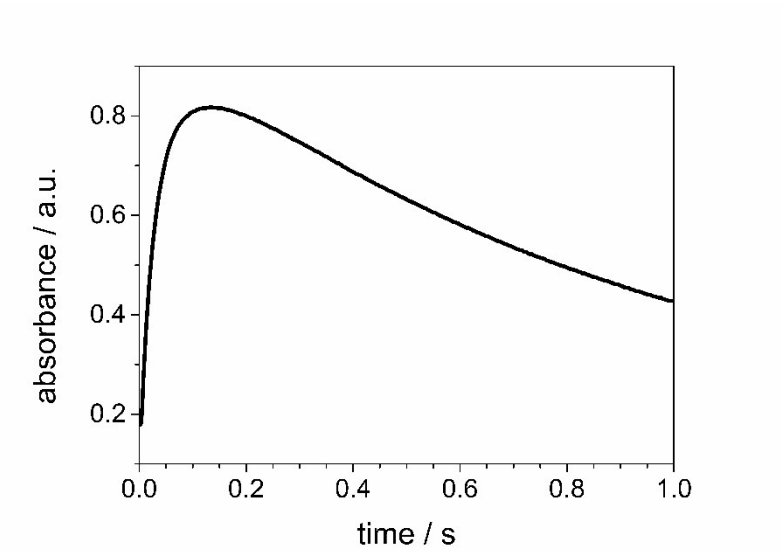

Figure S1: Extinction measured by UV spectroscopy versus time at 295 K. Initial copper(I) complex concentration = 3 x 10^{-4} mol/L. Formation and decay of the bis(μ-oxo) copper(III) species $k_{formation}$ = 10 s^{-1}, k_{decay} = 1.57 s^{-1}

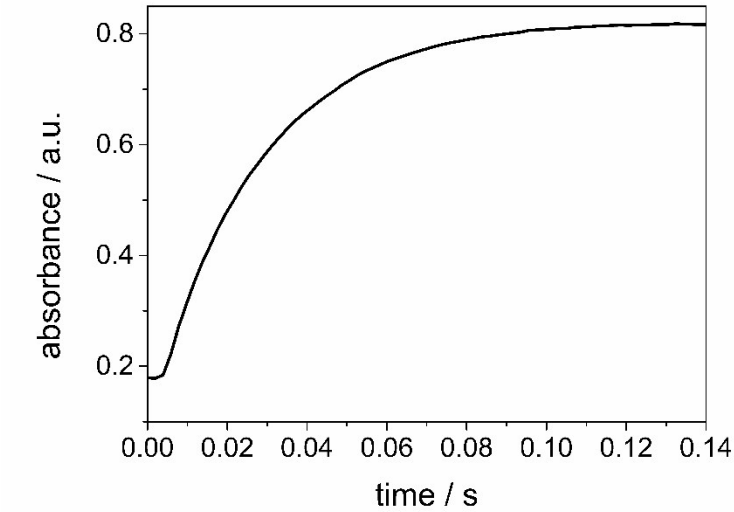

Figure S2: Extinction measured by UV spectroscopy versus time at 295 K. Initial copper(I) complex concentration = 3 x 10^{-4} mol/L. Formation and decay of the bis(μ-oxo) copper(III) species $k_{formation}$ = 10 s^{-1}, k_{decay} = 1.57 s^{-1}

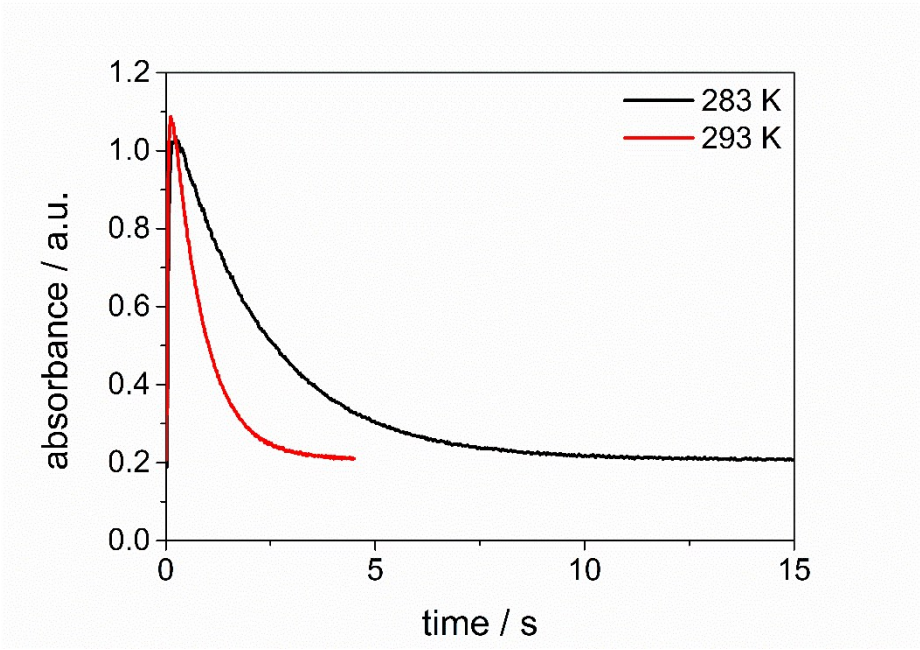

Figure S3: Absorption measured by UV spectroscopy versus time at a temperature range of 283 to 293 K. Initial copper(I) complex concentration = 3 x 10^{-4} mol/L.

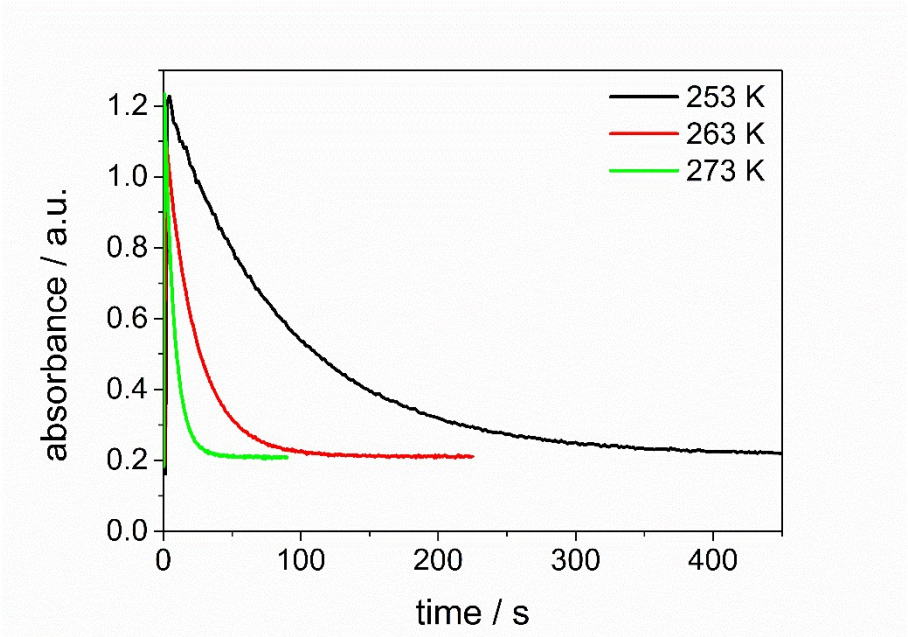

Figure S4: Extinction measured by UV spectroscopy versus time at a temperature range of 253 to 273 K. Initial copper(I) complex concentration = 3 x 10^{-4} mol/L.

Systematic derivation of the fitting equation

Reaction

$$2\,Cu(I) + O_2 \xrightarrow{k_1} Cu(III) \xrightarrow{k_2} Cu(II)$$

Reaction rates

$r_1 = k_1[Cu(I)]$

$r_2 = k_2[Cu(III)]$

Differential equations

$$\frac{d[Cu(I)]}{dt} = -r_1 = -k_1[Cu(I)]$$

$$\frac{d[Cu(III)]}{dt} = r_1 - r_2 = k_1[Cu(I)] - k_2[Cu(III)]$$

$$\frac{d[Cu(II)]}{dt} = r_2 = k_2[Cu(III)]$$

Mass balance

$$\frac{1}{2}[Cu(I)_0] = \frac{1}{2}[Cu(I)] + [Cu(II)] + [Cu(III)]$$

Solution

$$[Cu(I)] = [Cu(I)_0]e^{-k_1 t}$$

$$[Cu(III)] = [Cu(I)_0]\frac{k_1}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

$$[Cu(II)] = \frac{1}{2}[Cu(I)_0] - [Cu(I)] - [Cu(III)] = [Cu(I)_0]\left[\frac{1}{2} - \frac{(3k_1 - k_2)e^{-k_1 t} - 2k_1 e^{-k_2 t}}{2(k_1 - k_2)}\right]$$

Without Simplifications

Absorbance at 395 nm

$$Abs_{395} = Abs_{395,\ Cu(III)} + Abs_{395,\ Cu(II)}$$

Linear correlation of absorbance and concentration

$$c_i = B_i\, Abs + D_i$$

$$Abs_{395} = \frac{[Cu(III)] - D_1}{B_1} + \frac{[Cu(II)] - D_2}{B_2} = \frac{[Cu(III)] - D_1}{B_1} - \frac{\frac{1}{2}[Cu(I)_0] - [Cu(III)] - \frac{1}{2}[Cu(I)] - D_2}{B_2}$$

$$Abs_{395} = [Cu(III)]\left(\frac{1}{B_1} - \frac{1}{B_2}\right) + \frac{[Cu(I)_0]}{2B_2} - \frac{D_1}{B_1} - \frac{D_2}{B_2} - \frac{[Cu(I)]}{2B_2}$$

$$Abs_{395} = \left(\frac{1}{B_1} - \frac{1}{B_2}\right)[Cu(I)_0]\frac{k_1}{k_2 - k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right] + \frac{[Cu(I)_0]}{2B_2} - \frac{D_1}{B_1} - \frac{D_2}{B_2} - \frac{1}{2B_2}[Cu(I)_0]e^{-k_1 t}$$

$$Abs_{395} = e^{-k_1 t}\underbrace{\left[\left(\frac{1}{B_1} - \frac{1}{B_2}\right)[Cu(I)_0]\frac{k_1}{k_2 - k_1} - \frac{1}{2B_2}[Cu(I)_0]\right]}_{D} - \underbrace{\left(\frac{1}{B_1} - \frac{1}{B_2}\right)[Cu(I)_0]\frac{k_1}{k_2 - k_1}}_{E} e^{-k_2 t} + \underbrace{\frac{[Cu(I)_0]}{2B_2} - \frac{D_1}{B_1} - \frac{D_2}{B_2} - \frac{1}{2B_2}}_{F}$$

$$Abs_{395} = De^{-k_1 t} + Ee^{-k_2 t} + F$$

With Simplification: Fit for $t > t^*$, viz. as soon as all Cu(I) is consumed

$$\rightarrow r_1 = 0 \quad und \quad \frac{1}{2}[Cu(I)_0] = [Cu(III)] + [Cu(II)]$$

Differential equation

$$\frac{d[Cu(III)]}{dt} = -r_2 = -k_2[Cu(III)]$$

Solution: Integration lower bond t*

$$\ln([Cu(III)]) = \underbrace{-k_2 t}_{+ k_2 t^* + \ln([Cu(III)]_{t^*})} \underbrace{}_{= \ln(A_1) = const}$$

$$[Cu(III)] = e^{-k_2 t} A_1$$

Absorbance

$$Abs_{395} = \frac{[Cu(III)] - D_1}{B_1} + \frac{[Cu(II)] - D_2}{B_2} = \frac{[Cu(III)] - D_1}{B_1} - \frac{\frac{1}{2}[Cu(I)_0] - [Cu(III)] - D_2}{B_2}$$

$$Abs_{395} = [Cu(III)]\left(\frac{1}{B_1} - \frac{1}{B_2}\right) + \frac{[Cu(I)_0]}{2B_2} - \frac{D_1}{B_1} - \frac{D_2}{B_2}$$

$$Abs_{395} = \underbrace{\left(\frac{1}{B_1} - \frac{1}{B_2}\right)A_1}_{= A' = const} e^{-k_2 t} + \underbrace{\frac{[Cu(I)_0]}{2B_2} - \frac{D_1}{B_1} - \frac{D_2}{B_2}}_{= B' = const}$$

$$Abs_{395} = A' e^{-k_2 t} + B'$$