

1 **Supplementary information for the manuscript “Ascorbate Oxidation by**  
2 **Iron, Copper and Reactive Oxygen Species: Review, Model Development,**  
3 **and Derivation of Key Rate Constants”**

4 Jiaqi Shen,<sup>1</sup> Paul T. Griffiths,<sup>2</sup> Steven J. Campbell,<sup>3</sup> Battist Utinger,<sup>3</sup> Markus Kalberer<sup>2,3</sup> and  
5 Suzanne E. Paulson<sup>1\*</sup>

6 <sup>1</sup>Department of Atmospheric and Oceanic Sciences, University of California at Los Angeles, Los  
7 Angeles, CA USA 90095-1565

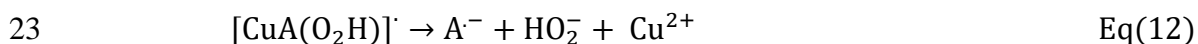
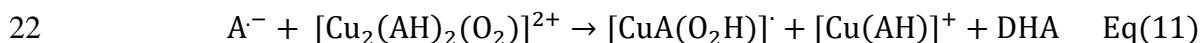
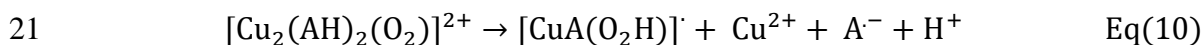
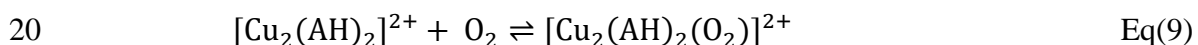
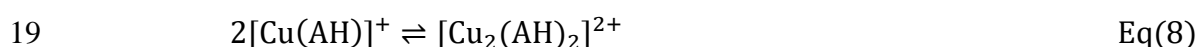
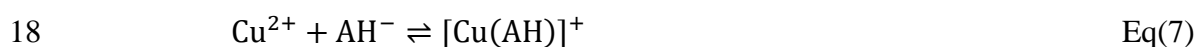
8 <sup>2</sup>Department of Chemistry, Cambridge University, Lensfield Rd. Cambridge CB2 1EW UK

9 <sup>3</sup>Department of Environmental Sciences, University of Basel, Klingelbergstrasse 27, 4056 Basel,  
10 Switzerland

11  
12 \*Corresponding Author. paulson@atmos.ucla.edu; Telephone: (310) 206 4442; fax (310) 206  
13 5219  
14

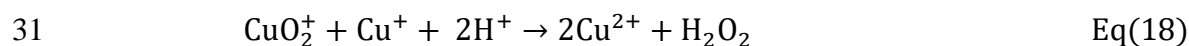
15 **1. Additional Mechanisms for Cu Reactions with Ascorbic Acid Proposed in the**  
16 **Literature**

17 **Jameson and Blackburn<sup>1</sup>**



26

27 **Scheme C Shtamm et al.<sup>2</sup>**



32 **2. Fluorescence Measurement**

33 The fluorescent product 3-(1,2-dihydroxyethyl)-fluoro[3,4-b]quinoxaline-1-one (DFQ) is excited  
34 at  $\lambda = 365$  nm by a high-power UV LED, with a strong peak emission at  $\lambda_{\text{max}} = 430$  nm measured  
35 using optical fibers (Thorlabs M93L01) coupled to a femtowatt photoreceiver (Thorlabs type  
36 PDF10A) with a cyan fluorescent protein excitation filter (Thorlabs type MF434-17), which only  
37 transmits light between 423 and 445 nm. For pH 7 the mixture containing DFQ is measured with  
38 a spectrometer (Ocean Optics QE Pro) with an integration time of 1000 ms and an integration  
39 interval from 425 to 435 nm.

40 **3. Copper – ROS Reactions**

41  $\text{OH}\cdot$  production from Cu(II) is very sensitive to  $\text{Cu(II)} + \text{H}_2\text{O}_2$  (R77) which produces Cu(I) and  
42 the reactions between Cu(I) and  $\text{H}_2\text{O}_2$  (R80-81) which together control the formation of  $\text{OH}\cdot$ . Pham  
43 et al.<sup>3</sup> found a high rate constant for R77 of  $460 \text{ M}^{-1}\text{s}^{-1}$ , but most studies agree that the rate constant  
44 for copper and copper hydroxide species is  $< 1 \text{ M}^{-1}\text{s}^{-1}$ <sup>4-7</sup> and  $70 \text{ M}^{-1}\text{s}^{-1}$  for the Cu(II)-chloro  
45 complex;<sup>5</sup> we adopt these values here (Tab. 2). Similar to the iron Fenton reaction, Cu(III) is also  
46 thought to be a possible product of the reaction between Cu(I) and  $\text{H}_2\text{O}_2$  with a rate constant of  $61$   
47  $\text{M}^{-1}\text{s}^{-1}$ ;<sup>3</sup> only an upper limit rate constant ( $100 \text{ M}^{-1}\text{s}^{-1}$ ) could be found for the reaction of Cu(I) and  
48  $\text{H}_2\text{O}_2 \rightarrow \text{OH}\cdot$  (R80<sup>8</sup>). Relatively larger uncertainties exist in the copper Fenton reaction than iron.

49 Other potential sources of error can be the uncertainties of the rate law associated with the  
50 background ions (see manuscript).

51

52 **Table S1. Rate constant for OH· + AH<sub>2</sub>/AH<sup>-</sup>**

pH	Rate constant (M <sup>-1</sup> s <sup>-1</sup> )	Reference
1.0	7.9 × 10 <sup>9*</sup>	Redpath and Willson <sup>9</sup>
7.0	10 <sup>9</sup>	
7.4	1.1 × 10 <sup>10*</sup>	Buettner and Schafer <sup>10</sup>
1.0	7.2 × 10 <sup>9</sup>	Bielski <sup>11</sup>
1.5	4.5 × 10 <sup>9</sup>	Bielski <sup>11</sup>
7.0	7.0 × 10 <sup>9</sup>	
7.0	1.1 × 10 <sup>10</sup>	Bielski <sup>11</sup>
11.0	4.1 × 10 <sup>9</sup>	Bielski <sup>11</sup>
7.4	1.1 × 10 <sup>10</sup>	Lakey et al. <sup>7</sup>

53 \* Rate constants adopted in this study.

54 **Table S2. Reaction conditions**

Final reaction conditions: reaction coil-1				
	pH 2.8		pH 7	
Ascorbic acid concentration	100	μM	200	μM
<b>Flow rates:</b>				
Ascorbic acid	1.1	ml/min	0.5	ml/min
DHA/Cu(II)/Fe(II)/Fe(III)	1.1	ml/min	0.5	ml/min

<b>Temp:</b>	37	°C	37	°C
<b>Reaction time:</b>	20	min	20	min
<b>Final reaction conditions: reaction coil-2</b>				
Ascorbic acid concentration	67	μM	100	μM
oPDA concentration	15	mM	10	mM
<b>Flow rates:</b>				
Ascorbic acid	1.1	ml/min	0.5	ml/min
DHA/Cu(II)/Fe(II)/Fe(III)	1.1	ml/min	0.5	ml/min
oPDA	1.1	ml/min	1	ml/min
<b>Temp:</b>	20	°C	37	°C
<b>Reaction time:</b>	10	min	5	min

55

56 **References**

- 57
- 58 1. Jameson, R.F. and Blackburn, N.J., Role of copper dimers and the participation of copper  
59 (III) in the copper-catalysed autoxidation of ascorbic acid. Part II. Kinetics and mechanism  
60 in 0.100 mol dm<sup>-3</sup> potassium nitrate. *Journal of the Chemical Society, Dalton*  
61 *Transactions*, 1976a(6): p. 534-541.
- 62 2. Shtamm, E., Purmal, A., and Skurlatov, Y.I., Mechanism of catalytic ascorbic acid  
63 oxidation system Cu<sup>2+</sup>–ascorbic acid–O<sub>2</sub>. *International Journal of Chemical Kinetics*,  
64 1979. **11**(5): p. 461-494.
- 65 3. Pham, A.N., Xing, G., Miller, C.J., and Waite, T.D., Fenton-like copper redox chemistry  
66 revisited: hydrogen peroxide and superoxide mediation of copper-catalyzed oxidant  
67 production. *Journal of catalysis*, 2013. **301**: p. 54-64.
- 68 4. Zhou, S., Yu, Y., Sun, J., Zhu, S., and Deng, J., Oxidation of microcystin-LR by copper  
69 (II) coupled with ascorbic acid: Kinetic modeling towards generation of H<sub>2</sub>O<sub>2</sub>. *Chemical*  
70 *Engineering Journal*, 2018. **333**: p. 443-450.
- 71 5. Wang, Z., *et al.*, Accelerated oxidation of 2, 4, 6-trichlorophenol in Cu (II)/H<sub>2</sub>O<sub>2</sub>/Cl-  
72 system: A unique “halotolerant” Fenton-like process? *Environment international*, 2019.  
73 **132**: p. 105128.
- 74 6. Lee, H., *et al.*, Activation of oxygen and hydrogen peroxide by copper (II) coupled with  
75 hydroxylamine for oxidation of organic contaminants. *Environmental science &*  
76 *technology*, 2016. **50**(15): p. 8231-8238.
- 77 7. Lakey, P.S., *et al.*, Chemical exposure-response relationship between air pollutants and  
78 reactive oxygen species in the human respiratory tract. *Scientific reports*, 2016. **6**: p. 32916.
- 79 8. Pham, A.N., Rose, A.L., and Waite, T.D., Kinetics of Cu (II) reduction by natural organic  
80 matter. *The Journal of Physical Chemistry A*, 2012. **116**(25): p. 6590-6599.
- 81 9. Redpath, J. and Willson, R., Reducing compounds in radioprotection and radio-  
82 sensitization: Model experiments using ascorbic acid. *International Journal of Radiation*  
83 *Biology and Related Studies in Physics, Chemistry and Medicine*, 1973. **23**(1): p. 51-65.
- 84 10. Buettner, G.R. and Schafer, F.Q., Ascorbate (Vitamin C), its antioxidant chemistry. *Society*  
85 *For Free Radical Biology and Medicine*, 2001: p. 20.
- 86 11. Bielski, B.H., Chemistry of ascorbic acid radicals. *Adv. Chem. Ser.;*(United States), 1982.  
87 **200**.
- 88