

Supporting Information for “Atmospheric protein chemistry influenced by anthropogenic air pollutants: nitration and oligomerization upon exposure to ozone and nitrogen dioxide”

Faraday Discussions

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Table S1 The chemical mechanism with 19 equations and the corresponding parameters used in the kinetic model for the reactions of proteins with O₃ and NO₂ at 45% RH, 96% RH and aqueous solutions. The bulk diffusion coefficients of O₃ and NO₂ were estimated to be $1.9 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at 45% RH and $1.0 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 96% RH; self-diffusion coefficients of protein were estimated to be $9.0 \times 10^{-21} \text{ cm}^2 \text{ s}^{-1}$ at 45% RH and $1.0 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ at 96% RH. Note that reactions on the surface were also included for the flow tube experiments with rate constants determined using the following equation: $k_{\text{surface}} (\text{cm}^2 \text{ s}^{-1}) = 1 \times 10^4 \times k_{\text{bulk}} (\text{cm}^3 \text{ s}^{-1})$.

No.	Equation	Parameters		
		45% RH	96% RH	Aqueous
	Total BSA = $x_I \text{ AA}_1 + (1-x_I) \text{ AA}_2$	$x_I = 0.56$	$x_I = 0.65$	$x_I = 0.69$
R1	$\text{O}_3 + \text{AA}_1 \rightarrow c_I \text{ ROI-1} + (1-c_I) \text{ oxidized monomer}$	$k_I = 3.41 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ $c_I = 0.97$	$k_I = 5.99 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ $c_I = 0.99$	$k_I = 5.00 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ $c_I = 0.97$
R2	$\text{O}_3 + \text{AA}_2 \rightarrow c_2 \text{ ROI-2} + (1-c_2) \text{ oxidized monomer}$	$k_2 = 4.55 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ $c_2 = 0.15$	$k_2 = 3.83 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ $c_2 = 0.25$	$k_2 = 8.32 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ $c_2 = 0.13$
R3	$\text{ROI-1} + \text{ROI-1} \rightarrow x_2 \text{ dimer}_1 + (1-x_2) \text{ dimer}_2$	$k_3 = 4.26 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$ $x_2 = 0.85$	$k_3 = 6.11 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$ $x_2 = 0.84$	$k_3 = 3.45 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ $x_2 = 0.54$
R4	$\text{ROI-1} + \text{NO}_2 \rightarrow \text{nitrated monomer}$	$k_4 = 5.00 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$	$k_4 = 5.00 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$	$k_4 = 5.00 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$
R5	$\text{ROI-1} \rightarrow \text{AA}_1$	$k_5 = 1.98 \times 10^{-8} \text{ s}^{-1}$	$k_5 = 9.38 \times 10^{-8} \text{ s}^{-1}$	$k_5 = 6.95 \times 10^{-4} \text{ s}^{-1}$
R6	$\text{ROI-2} + \text{NO}_2 \rightarrow \text{nitrated monomer}$	$k_6 = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k_6 = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k_6 = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
R7	$\text{dimer}_1 + \text{O}_3 \rightarrow c_3 \text{ ROI-3} + (1-c_3) \text{ oxidized dimer}$	$k_7 = 1.64 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ $c_3 = 0.57$	$k_7 = 1.81 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ $c_3 = 0.78$	$k_7 = 1.01 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ $c_3 = 0.67$
R8	$\text{dimer}_2 + \text{O}_3 \rightarrow c_4 \text{ ROI-4} + (1-c_4) \text{ oxidized dimer}$	$k_8 = 9.94 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ $c_4 = 0.13$	$k_8 = 9.94 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ $c_4 = 0.14$	$k_8 = 1.41 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ $c_4 = 0.14$
R9	$\text{ROI-3} + \text{ROI-3} \rightarrow \text{tetramer}$	$k_9 = 9.76 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$	$k_9 = 8.88 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}$	$k_9 = 2.29 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$
R10	$\text{ROI-1} + \text{ROI-3} \rightarrow x_3 \text{ trimer}_1 + (1-x_3) \text{ trimer}_2$	$k_{10} = 4.80 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ $x_3 = 0.80$	$k_{10} = 4.77 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ $x_3 = 0.80$	$k_{10} = 3.75 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ $x_3 = 0.80$

R11	ROI-3 + NO ₂ → nitrated dimer	$k_{11} = 5.32 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$	$k_{11} = 6.18 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$	$k_{11} = 2.77 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$
R12	ROI-3 → dimer ₁	$k_{12} = 7.63 \times 10^{-9} \text{ s}^{-1}$	$k_{12} = 9.58 \times 10^{-8} \text{ s}^{-1}$	$k_{12} = 1.06 \times 10^{-5} \text{ s}^{-1}$
R13	ROI-4 + NO ₂ → nitrated dimer	$k_{13} = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k_{13} = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k_{13} = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
R14	trimer ₁ + O ₃ → c ₅ ROI-5 + (1-c ₅) oxidized trimer	$k_{14} = 1.00 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ c ₅ = 0.15	$k_{14} = 1.00 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ c ₅ = 0.15	$k_{14} = 1.00 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ c ₅ = 0.15
R15	trimer ₂ + O ₃ → c ₆ ROI-6 + (1-c ₆) oxidized trimer	$k_{15} = 1.00 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ c ₆ = 0.15	$k_{15} = 1.00 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ c ₆ = 0.15	$k_{15} = 1.00 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ c ₆ = 0.15
R16	ROI-1 + ROI-5 → tetramer	$k_{16} = 5.00 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$	$k_{16} = 5.00 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$	$k_{16} = 5.00 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$
R17	ROI-5 + NO ₂ → nitrated trimer	$k_{17} = 5.00 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$	$k_{17} = 5.00 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$	$k_{17} = 5.00 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$
R18	ROI-5 → trimer ₁	$k_{18} = 1.00 \times 10^{-7} \text{ s}^{-1}$	$k_{18} = 1.00 \times 10^{-7} \text{ s}^{-1}$	$k_{18} = 1.00 \times 10^{-7} \text{ s}^{-1}$
R19	ROI-6 + NO ₂ → nitrated trimer	$k_{19} = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k_{19} = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$	$k_{19} = 1.00 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$

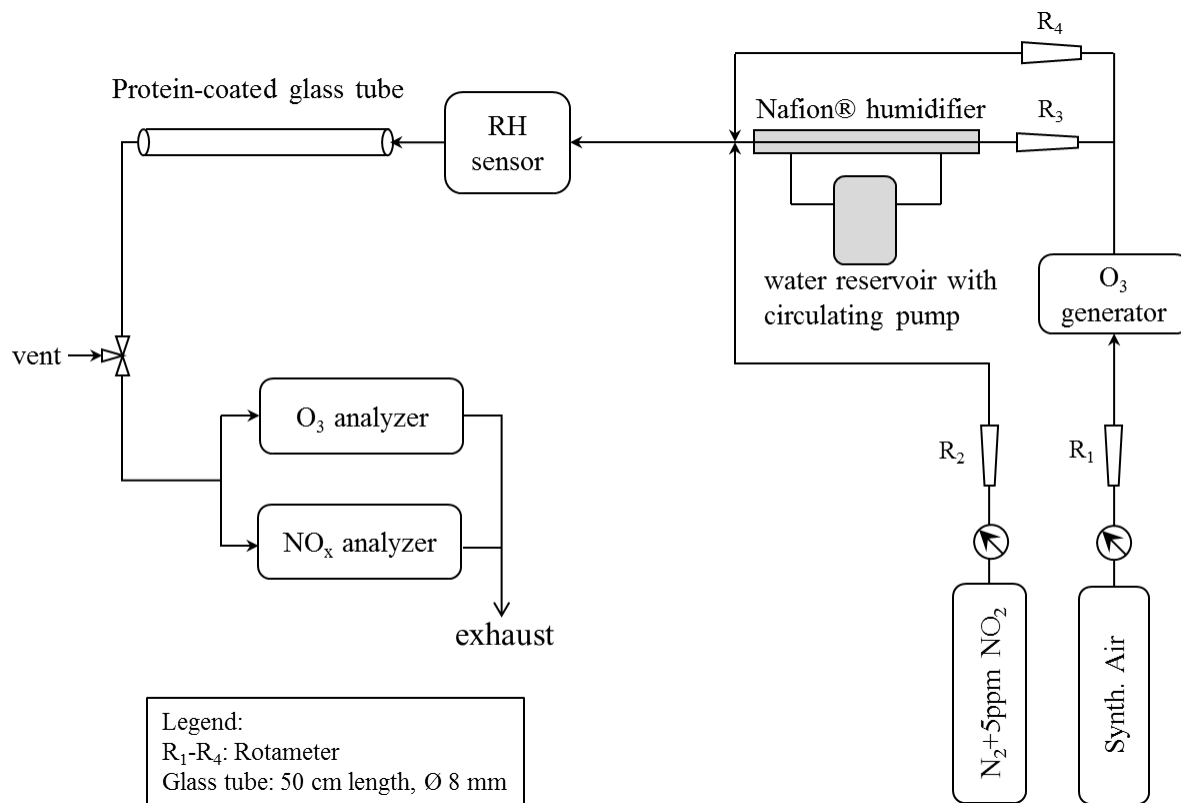


Fig. S1 Experimental setup for protein exposure to O₃/NO₂.

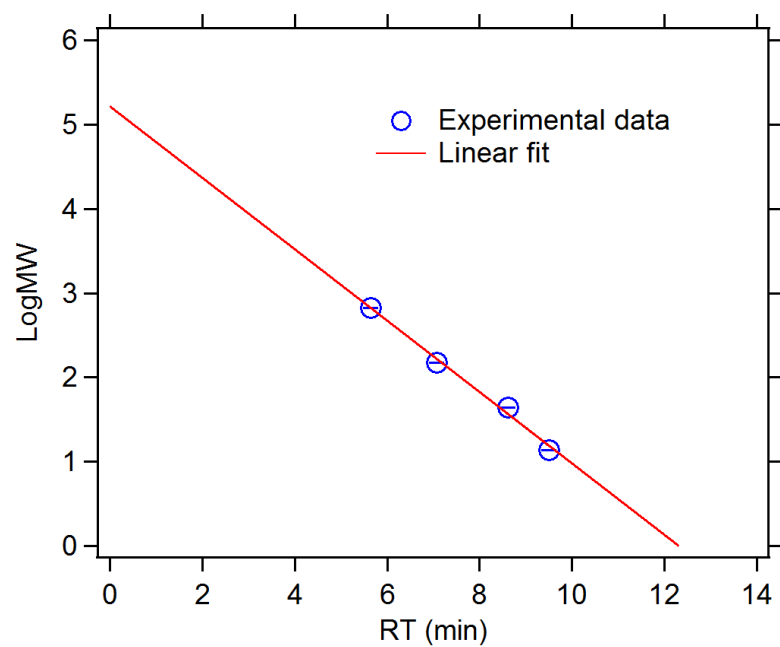


Fig. S2 Calibration curve plotting the logarithm of molecular weight (Log MW) against retention time (RT) of the protein standard mix. The fitting equation was $y = -0.42x + 5.21$, $R^2 = 0.99$.