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 O_3 and NO_2 at 45% RH, 96% RH and aqueous solutions. The bulk diffusion coefficients of O_3 and NO_2 were estimated to be 1.9×10^{-10} $cm^2\ s^{-1}$ at 45% RH and 1.0×10^{-9} $cm^2\ s^{-1}$ at 96% RH; self-diffusion coefficients of protein were estimated to be 9.0×10^{-21} $cm^2\ s^{-1}$ at 45% RH and 1.0×10^{-18} $cm^2\ s^{-1}$ 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: $k_{surface}$ ($cm^2\ s^{-1}$) = $1 \times 10^4 \times k_{bulk}$ ($cm^3\ s^{-1}$).

No.	Equation	Parameters		
		45% RH	96% RH	Aqueous
	Total BSA = x_1 AA_1 + (1-x_1) AA_2	$x_1 = 0.56$	$x_1 = 0.65$	$x_1 = 0.69$
R1	O_3 + AA_1 → c_1 ROI-1 + (1-c_1) oxidized monomer	$k_1 = 3.41 \times 10^{-15}$ $cm^3\ s^{-1}$ $c_1 = 0.97$	$k_1 = 5.99 \times 10^{-15}$ $cm^3\ s^{-1}$ $c_1 = 0.99$	$k_1 = 5.00 \times 10^{-14}$ $cm^3\ s^{-1}$ $c_1 = 0.97$
R2	O_3 + AA_2 → c_2 ROI-2 + (1-c_2) oxidized monomer	$k_2 = 4.55 \times 10^{-15}$ $cm^3\ s^{-1}$ $c_2 = 0.15$	$k_2 = 3.83 \times 10^{-14}$ $cm^3\ s^{-1}$ $c_2 = 0.25$	$k_2 = 8.32 \times 10^{-16}$ $cm^3\ s^{-1}$ $c_2 = 0.13$
R3	ROI-1 + ROI-1 → x_2 $dimer_1$ + (1- x_2) $dimer_2$	$k_3 = 4.26 \times 10^{-19}$ $cm^3\ s^{-1}$ $x_2 = 0.85$	$k_3 = 6.11 \times 10^{-19}$ $cm^3\ s^{-1}$ $x_2 = 0.84$	$k_3 = 3.45 \times 10^{-20}$ $cm^3\ s^{-1}$ $x_2 = 0.54$
R4	ROI-1 + NO_2 → nitrated monomer	$k_4 = 5.00 \times 10^{-19}$ $cm^3\ s^{-1}$	$k_4 = 5.00 \times 10^{-19}$ $cm^3\ s^{-1}$	$k_4 = 5.00 \times 10^{-19}$ $cm^3\ s^{-1}$
R5	ROI-1 → AA_1	$k_5 = 1.98 \times 10^{-8}$ s^{-1}	$k_5 = 9.38 \times 10^{-8}$ s^{-1}	$k_5 = 6.95 \times 10^{-4}$ s^{-1}
R6	ROI-2 + NO_2 → nitrated monomer	$k_6 = 1.00 \times 10^{-13}$ $cm^3\ s^{-1}$	$k_6 = 1.00 \times 10^{-13}$ $cm^3\ s^{-1}$	$k_6 = 1.00 \times 10^{-13}$ $cm^3\ s^{-1}$
R7	$dimer_1$ + O_3 → c_3 ROI-3 + (1-c_3) oxidized dimer	$k_7 = 1.64 \times 10^{-13}$ $cm^3\ s^{-1}$ $c_3 = 0.57$	$k_7 = 1.81 \times 10^{-13}$ $cm^3\ s^{-1}$ $c_3 = 0.78$	$k_7 = 1.01 \times 10^{-15}$ $cm^3\ s^{-1}$ $c_3 = 0.67$
R8	$dimer_2$ + O_3 → c_4 ROI-4 + (1-c_4) oxidized dimer	$k_8 = 9.94 \times 10^{-15}$ $cm^3\ s^{-1}$ $c_4 = 0.13$	$k_8 = 9.94 \times 10^{-15}$ $cm^3\ s^{-1}$ $c_4 = 0.14$	$k_8 = 1.41 \times 10^{-15}$ $cm^3\ s^{-1}$ $c_4 = 0.14$
R9	ROI-3 + ROI-3 → tetramer	$k_9 = 9.76 \times 10^{-21}$ $cm^3\ s^{-1}$	$k_9 = 8.88 \times 10^{-21}$ $cm^3\ s^{-1}$	$k_9 = 2.29 \times 10^{-20}$ $cm^3\ s^{-1}$
R10	ROI-1 + ROI-3 → x_3 $trimer_1$ + (1- x_3) $trimer_2$	$k_{10} = 4.80 \times 10^{-20}$ $cm^3\ s^{-1}$ $x_3 = 0.80$	$k_{10} = 4.77 \times 10^{-20}$ $cm^3\ s^{-1}$ $x_3 = 0.80$	$k_{10} = 3.75 \times 10^{-20}$ $cm^3\ s^{-1}$ $x_3 = 0.80$

R11	ROI-3 + NO_2 → nitrated dimer	k_{11} = 5.32 × 10^{-18} cm^3 s^{-1}	k_{11} = 6.18 × 10^{-17} cm^3 s^{-1}	k_{11} = 2.77 × 10^{-19} cm^3 s^{-1}
R12	ROI-3 → $dimer_1$	k_{12} = 7.63 × 10^{-9} s^{-1}	k_{12} = 9.58 × 10^{-8} s^{-1}	k_{12} = 1.06 × 10^{-5} s^{-1}
R13	ROI-4 + NO_2 → nitrated dimer	k_{13} = 1.00 × 10^{-13} cm^3 s^{-1}	k_{13} = 1.00 × 10^{-13} cm^3 s^{-1}	k_{13} = 1.00 × 10^{-13} cm^3 s^{-1}
R14	$trimer_1$ + O_3 → c_5 ROI-5 + (1-c_5) oxidized trimer	k_{14} = 1.00 × 10^{-12} cm^3 s^{-1} c_5= 0.15	k_{14} = 1.00 × 10^{-12} cm^3 s^{-1} c_5= 0.15	k_{14} = 1.00 × 10^{-12} cm^3 s^{-1} c_5= 0.15
R15	$trimer_2$ + O_3 → c_6 ROI-6 + (1-c_6) oxidized trimer	k_{15} = 1.00 × 10^{-15} cm^3 s^{-1} c_6= 0.15	k_{15} = 1.00 × 10^{-15} cm^3 s^{-1} c_6= 0.15	k_{15} = 1.00 × 10^{-15} cm^3 s^{-1} c_6= 0.15
R16	ROI-1 + ROI-5 → tetramer	k_{16} = 5.00 × 10^{-20} cm^3 s^{-1}	k_{16} = 5.00 × 10^{-20} cm^3 s^{-1}	k_{16} = 5.00 × 10^{-20} cm^3 s^{-1}
R17	ROI-5 + NO_2 → nitrated trimer	k_{17} = 5.00 × 10^{-16} cm^3 s^{-1}	k_{17} = 5.00 × 10^{-16} cm^3 s^{-1}	k_{17} = 5.00 × 10^{-16} cm^3 s^{-1}
R18	ROI-5 → $trimer_1$	k_{18} = 1.00 × 10^{-7} s^{-1}	k_{18} = 1.00 × 10^{-7} s^{-1}	k_{18} = 1.00 × 10^{-7} s^{-1}
R19	ROI-6 + NO_2 → nitrated trimer	k_{19} = 1.00 × 10^{-13} cm^3 s^{-1}	k_{19} = 1.00 × 10^{-13} cm^3 s^{-1}	k_{19} = 1.00 × 10^{-13} cm^3 s^{-1}

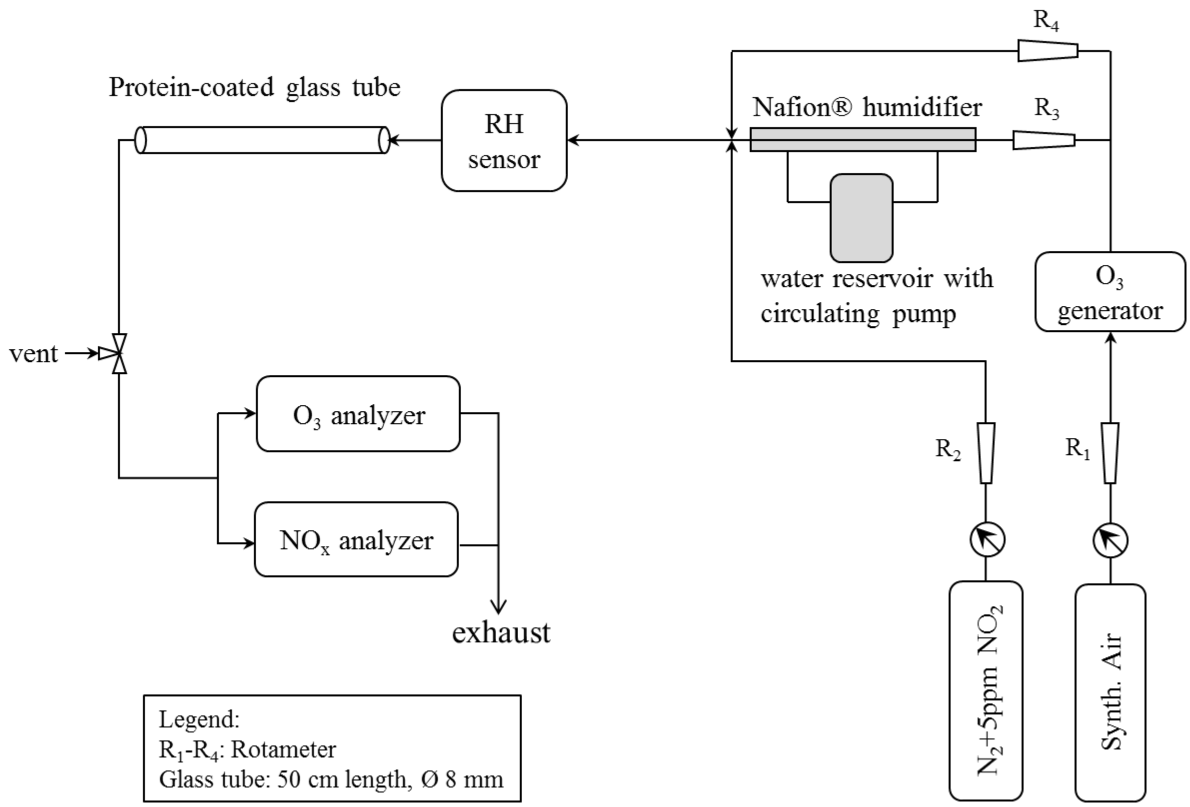

Fig. S1 Experimental setup for protein exposure to O_3/NO_2.

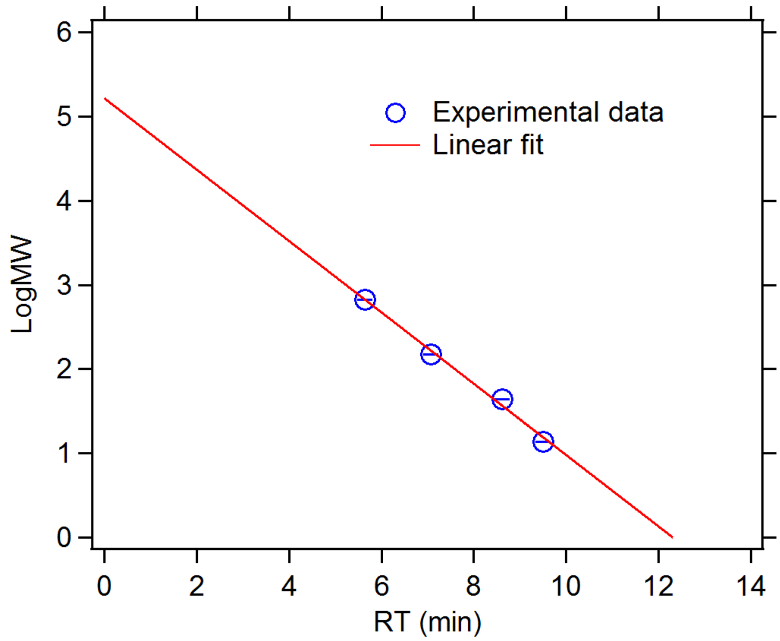

Fig. S2 Calibration curve plotting the logarithm of molecular weight (Log MW) against retention time (RT) of the protein standard mix. The fitting equation was y = -0.42x+5.21, R^2=0.99.