

Supporting Information

Experimental methods

Experiments were performed in the spraying chamber of a commercial electrospray ionization mass spectrometer (ESI-MS, HP-1100). Sodium halide solutions ($50 \mu\text{L min}^{-1}$) were pumped into the chamber through a grounded stainless steel needle injector ($100 \mu\text{m}$ internal diameter, $150 \mu\text{m}$ external diameter) concentric with a sheath ($250 \mu\text{m}$ internal diameter) issuing nebulizer gas at (0.5 L min^{-1}) (Figure SI_1.1).¹ The difference between the exit velocities of the liquid jet (10.6 cm s^{-1}) and nebulizer gas ($2.65 \times 10^4 \text{ cm s}^{-1}$) is so large that the drag imposed on the liquid breaks it apart into small droplets. The terminal velocities reached by the microdroplets thus created are $> 10^3 \text{ cm s}^{-1}$.⁴ Reaction times, τ , can thus be calculated as the transit times of microdroplets across the $\sim 0.5 \text{ cm}$ intersection with the ozone plume, i.e., $\tau < 1 \text{ ms}$. Ozone, produced by feeding O_2 (ultra-purity, Air Liquid America co.) to a commercial ozonizer (Ozone Solutions), was diluted tenfold in N_2 , and quantified by means of a UV-VIS meter (Agilent), prior to being admitted to the chamber (Figure SI_1.2). Ozone concentrations were calculated from absorbance measurements using recommended values for its absorption cross sections: $\sigma = 1.1 \times 10^{-17}$ (250 nm) and $\sigma = 3.9 \times 10^{-19}$ (300 nm) $\text{cm}^2 \text{ molecule}^{-1}$.⁵ The gases were then injected into the chamber, where they were further diluted tenfold in the countercurrent drying gas. We assumed that effective ozone concentrations in the plume traversed by the droplets were ten times smaller than those calculated from absorbance measurements. Gas flows were regulated by mass flow controllers (MKS).

Typical instrumental parameters were as follows: drying gas temperature: $350 \text{ }^\circ\text{C}$; nebulizer gas flow: 0.5 L min^{-1} ; collector capillary voltage: $+3.5 \text{ kV}$; fragmentor voltage: 80 V . All solutions were prepared in MilliQ water. NaI ($> 99 \%$, EM Science), NaBr ($> 99.5 \%$, EM Science) and NaCl ($> 99 \%$, J.T. Baker) were used as received.

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2. D. R. Hanson, *J. Phys. Chem. B* **101**, 4998 (1997).
3. J. Cheng, C. Vecitis, M. R. Hoffmann, A. J. Colussi, *J. Phys. Chem. B* **110**, 25598 (2006).
4. K. Kahen, K. Jorabchi, C. Gray, A. Montaser, *Anal. Chem.* **76**, 7194 (2004).
5. Sander, et al., Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 15, Jet Propulsion Laboratory, California Institute of Technology (2006).

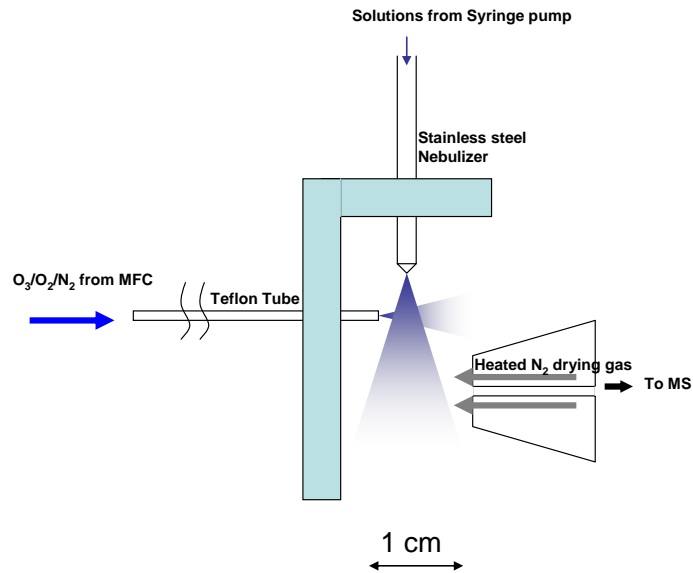


Figure SI_1.1: Schematic diagram of spraying chamber and $O_3(g)$ injection system.

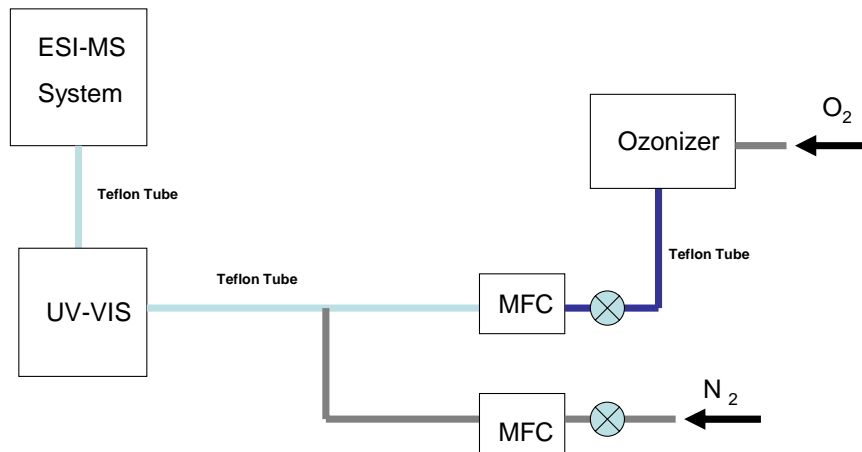


Figure SI_1.2: An overview of our experimental setup. MFC = Mass Flow Controller

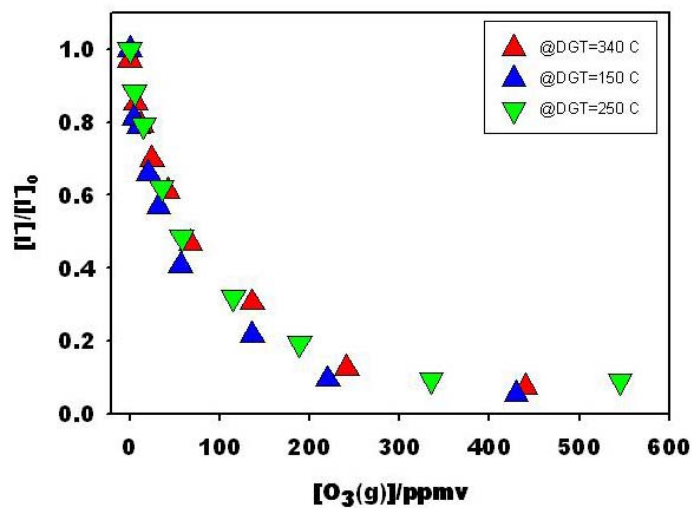


Fig. SI_2: Lack of drying gas temperature (DGT) effects on $[I + O_3(g)]$ kinetics. $[NaI]_0 = 30 \mu M$

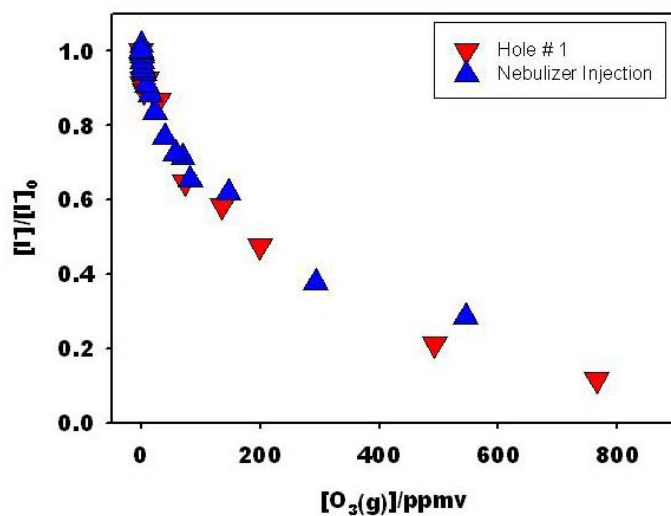


Fig. SI_3: Lack of $O_3(g)$ injection effects on $[I + O_3(g)]$ kinetics. $[NaI]_0 = 10 \mu M$. Hole # 1: $O_3(g)$ injected as shown in Figure SI_4A. Nebulizer injection: $O_3(g)$ mixed with the nebulizer gas

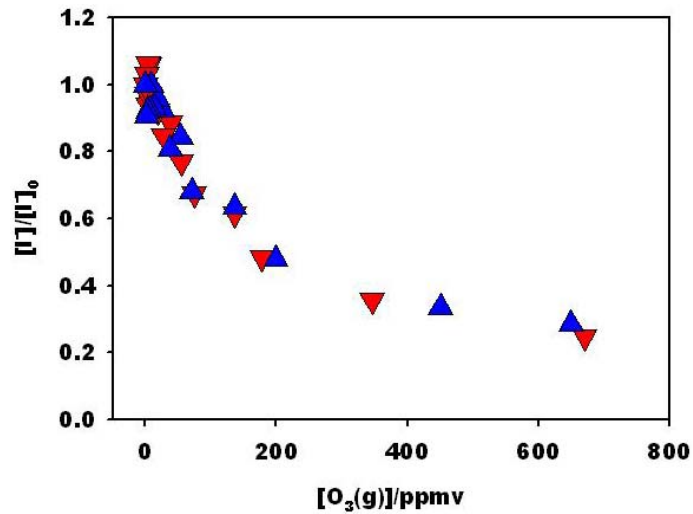


Fig. SI_4: Lack of collector capillary voltage effects on $[I^- + O_3(g)]$ kinetics. $[NaI]_0 = 30 \mu M$. Blue: 2.5 kV; Red: 1.5 kV.

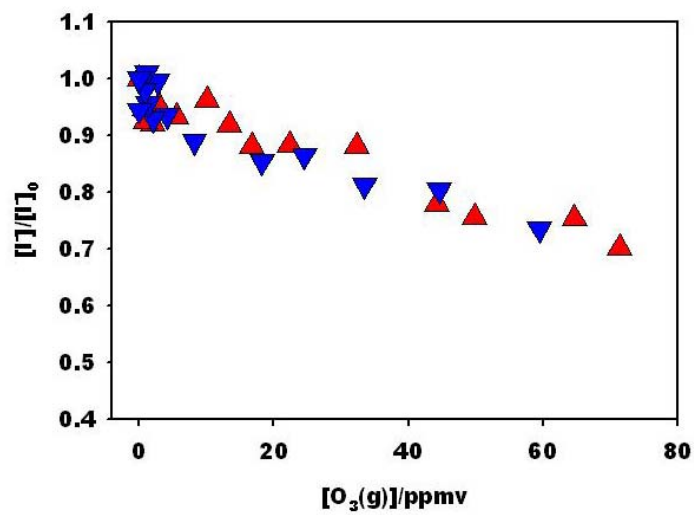


Fig. SI_5: Lack of pH effects on $[I^- + O_3(g)]$ kinetics. $[NaI]_0 = 10 \mu M$. Blue: pH 7; Red: pH 4, adjusted using $HClO_4$.

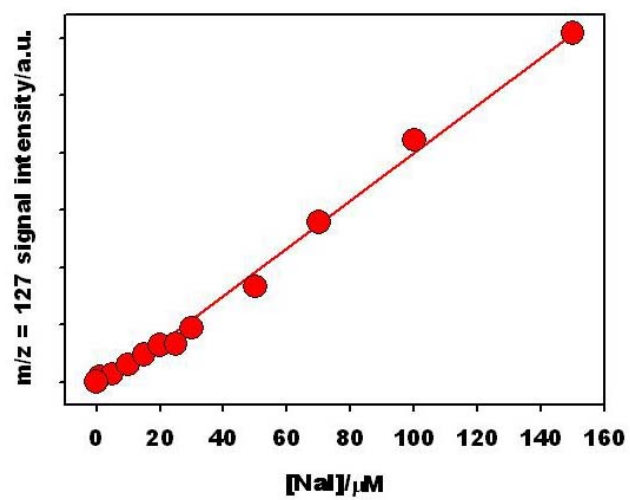


Fig. SI_6: Linear response of ESI-MS $m/z = 127$ signal to $[\text{NaI}]_0$ in the range 1 to 150 μM .