Supplement to: Technical note: Gas-phase nitrate radical generation via irradiation of aerated ceric ammonium nitrate mixtures

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S1 Theoretical analysis of the gas-phase $NO_3 + NO_3 \rightarrow N_2O_6$ reaction

To further explore the plausibility of N_2O_6 formation in this system, we conducted a theoretical investigation of the gas-phase $NO_3 + NO_3 \rightarrow N_2O_6$ reaction at T = 298 K and p = 1 atm. Quantum chemical calculations were performed using the Q-Chem 5.2 software package (Epifanovsky et al., 2021), and molecular geometries were obtained using the B3LYP density functional (Becke, 1993) and the 6-31G* basis set (Hariharan and Pople, 1973). All stationary points were refined by single point calculations applying the B3LYP density functional and the cc-pVTZ basis set (Dunning, 1989) as well as CCSD(T) (Jeziorski and Monkhorst, 1981) and the cc-pVTZ basis set. For $NO_3 + NO_3 \rightarrow N_2O_6$, the calculated enthalpy of reaction (ΔH_{rxn}) was -35.8 kcal mol^{-1} using the CCSD(T) method, and -21.9 kcal mol^{-1} using the B3LYP method. By comparison, we calculated ΔH_{rxn} values of -26.5 (CCSD(T)) and -18.1 (B3LYP) kcal mol^{-1} for the $NO_3 + NO_2 \rightarrow N_2O_5$ reaction; the corresponding energy change (ΔE_{rxn}) values agreed within 5% of previously obtained experimental and computational ΔE_{rxn} values for this reaction (Jitariu and Hirst, 2000; Glendening and Halpern, 2007). Thus, regardless of the quantum chemical method that was used, $NO_3 + NO_3 \rightarrow N_2O_6$ appears to be an exothermic reaction, even more so than $NO_3 + NO_2 \rightarrow N_2O_5$. While the reverse reaction $N_2O_6 \rightarrow 2\ NO_3$ is possible (although endothermic, as is $N_2O_5 \rightarrow NO_2 + NO_3$) our analysis suggests that the thermodynamically favored reaction pathway is $N_2O_6 \rightarrow N_2O_4 + O_2$, which had ΔH_{rxn} values ranging from -7.02 (CCSD(T)) to -6.15 (B3LYP) kcal mol^{-1}. By contrast, the reaction $N_2O_6 \rightarrow 2\ NO_2 + O_2$ had ΔH_{rxn} = 5.28 (CCSD(T)) and 5.58 (B3LYP) kcal mol^{-1}; however, because $N_2O_4 \rightarrow 2\ NO_2$ is fast (Poskrebyshev et al., 2001; Atkinson et al., 2004), the overall reaction $N_2O_6 \rightarrow 2\ NO_2 + O_2$ is the favored N_2O_6 removal pathway in the gas phase, and in solution may occur in addition to or instead of Reaction R4.

S2 Discussion of additional I^- CIMS signals

S2.1 IO_x^-, NO_2^-, NO_3^-, $IHNO_3^-$, $HNO_3NO_3^-$, and $IN_2O_7^-$

Figure S5 shows time series of I^-, IH_2O^-, IO^-, IO_2^-, NO_2^-, NO_3^-, $IHNO_3^-$, and $HNO_3NO_3^-$ obtained with the CIMS following irradiation of a mixture of 0.5 M CAN and 1.0 M $NaNO_3$. Signals of I^-, IH_2O^- and $IHNO_3^-$ decreased following irradiation of the CAN/$NaNO_3$ mixture, whereas IO^-, IO_2^-, NO_2^-, NO_3^-, and $HNO_3NO_3^-$ signals increased. One potential source of IO_x^- is I^- + O_3 reactions in the CIMS ion-molecule reactor (IMR); if this reaction was the sole source of IO_x^- here, we estimate an upper limit O_3 mixing ratio of approximately 15 ppbv present in the IMR (Dörich et al., 2021). NO_2^- is generated following the reaction of I^- and/or IO_x^- with HNO_2 (Abida and Osthoff, 2011), and NO_3^- is generated from the reaction of I^- and/or IO_x^- with multiple nitrogen oxides, including NO_3, HNO_3, HNO_4, and N_2O_5 (Huey et al., 1995; Veres et al., 2015; Dörich et al., 2021). Figure S5 additionally shows a time series of $IN_2O_7^-$, and Figures S6, S7, and S8 shows high-resolution CIMS spectra at m/Q = 235, 251, and 267. Given $IN_2O_7^-$:$IN_2O_5^-$ $\approx 10^{-3}$ coupled with similar $IN_2O_5^-$ and $IN_2O_7^-$ temporal profiles (Fig. S5), we hypothesize that N_2O_5 + IO_x^- reactions in the IMR were the primary source of $IN_2O_7^-$.

S2.2 $IN_2O_4^-$

$IN_2O_4^-$ was not detected with the CIMS following irradiation of aqueous $Ce^{(IV)}$, presumably because its hydrolysis rate was too fast (Park and Lee, 1988). In an attempt to decrease the hydrolysis rate, separate experiments were conducted in which the effluent of 40 g of irradiated solid CAN was sampled with the CIMS. At the sample sizes that were used, the solid CAN contained enough solvated HNO_3 and/or H_2O that its irradiation provided sufficient production of nitrogen oxides for CIMS detection. As shown in Figures S9, S10 and S11, CIMS NO_2^-, $IN_2O_4^-$, $I(HNO_2)_n^-$, and $(HNO_2)_nNO_3^-$ signals were significantly higher following irradiation at λ = 254 nm than at the other wavelengths, and Fig. S12 confirms that $IN_2O_4^-$ was the dominant ion signal at m/Q = 219. Taken together, these observations support our hypothesis that HNO_2 was generated following fast N_2O_4 hydrolysis in aqueous solution.
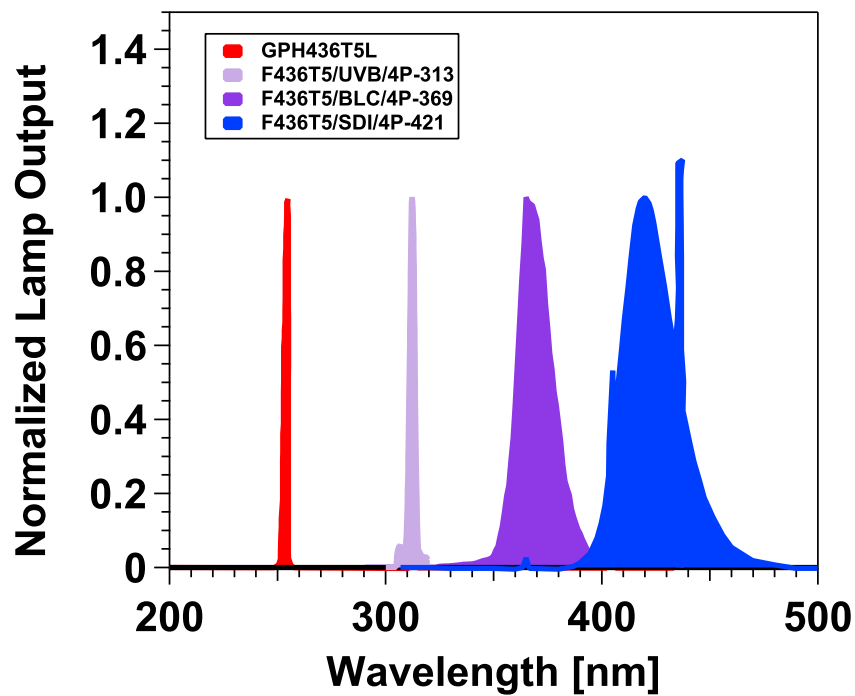
Figure S1. Normalized emission spectra for low-pressure GPH436T5L/4P, F436T5/UVB/4P-313, F436T5/BLC/4P-369, and F436T5/SDI/4P-421 mercury lamps used in this study. Spectra are provided by the manufacturer (GPH436T5L/4P: Light Sources Inc.; all others: LCD Lighting, Inc.)
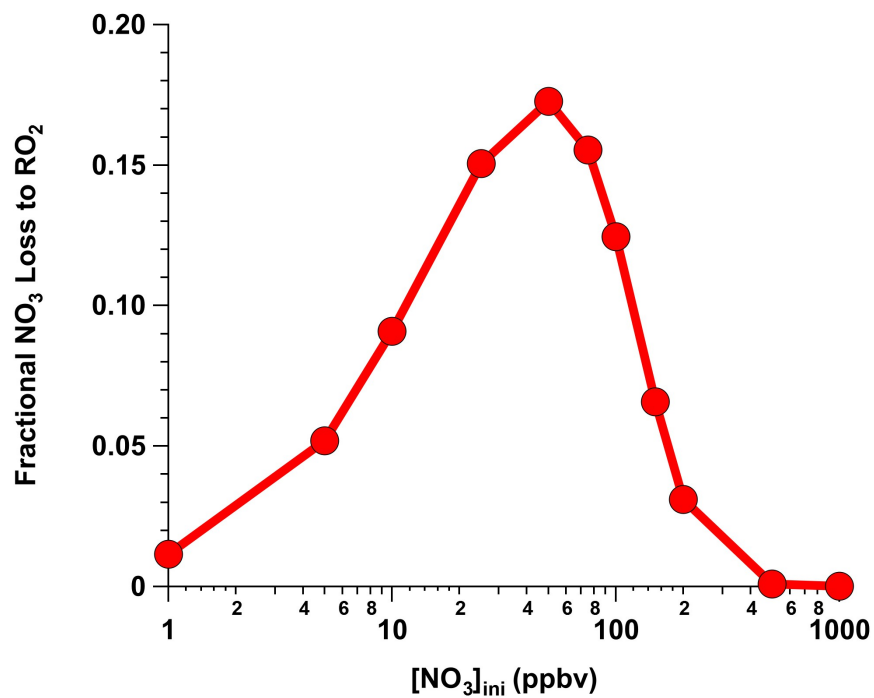
Figure S2. Fractional NO_3 consumption by RO_2 generated from VOC + NO_3 reactions during characterization studies described in Sect. 3.1.
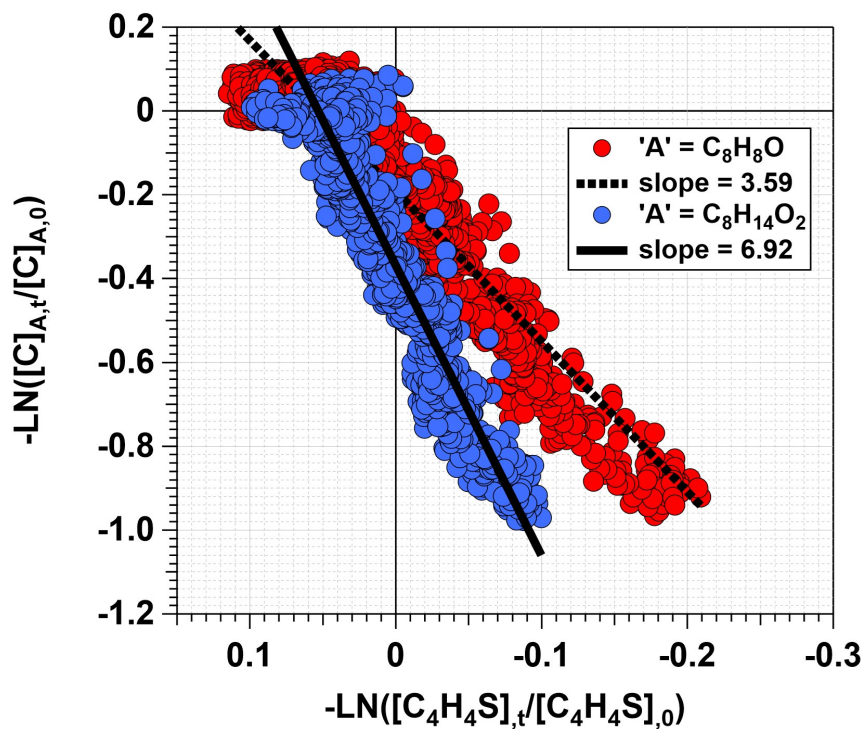
Figure S3. Relative rate coefficients obtained from Vocus measurements of acetonitrile (C_2H_3N, thiophene (C_4H_4S), 2,3-dibenzofuran (C_8H_8O), and cis-3-hexynyl-acetate ($C_8H_{14}O_2$) tracers used in characterization studies described in Sect. 3.1. Here, concentrations of C_4H_4S, C_8H_8O, and $C_8H_{14}O_2$ were first normalized to the C_2H_3N concentration to correct for changes in the syringe pump output over time and then normalized to the VOC concentration prior to NO_3 exposure. Literature relative rate coefficients obtained from kinetic data published by Atkinson (1991) and Atkinson et al. (1995).
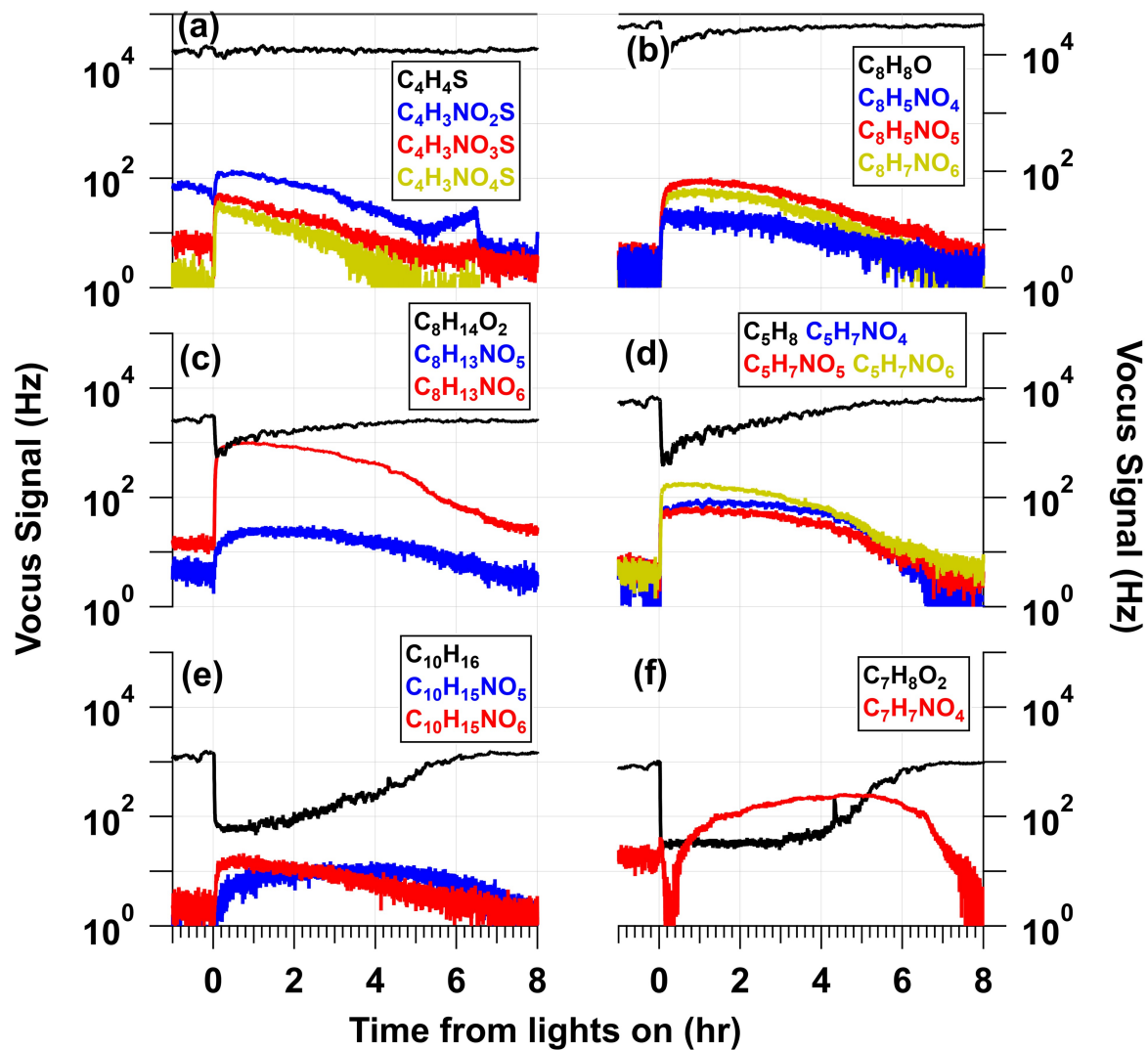
Figure S4. Time series of Vocus PTR ions measured following irradiation of a mixture containing 0.5 M CAN and 6.0 M HNO_3 mixture: **(a)** thiophene (C_4H_4S) and nitrothiophenes ($C_4H_3NO_{2-4}S$), **(b)** 2,3-dibenzofuran (C_8H_8O) and $C_8H_{5,7}NO_{4-6}$, **(c)** cis-3-hexynyl-acetate ($C_8H_{14}O_2$) and $C_8H_{13}NO_{5-6}$, **(d)** isoprene C_5H_8 and $C_5H_7NO_{4-6}$, **(e)** α-pinene ($C_{10}H_{16}$) and $C_{10}H_{15}NO_{5,6}$, and **(f)** guaiacol $C_7H_8O_2$ and nitroguiacol ($C_7H_7NO_4$).
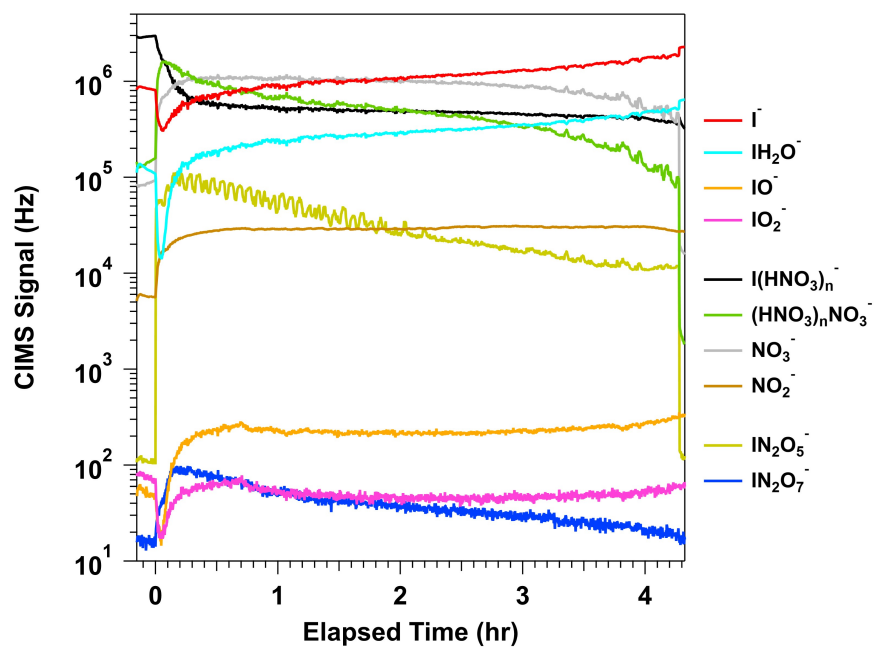
Figure S5. HR-ToF-CIMS time series of I^-, IH_2O^-, IO^-, IO_2^-, NO_2^-, NO_3^-, $IHNO_3^-$, and $HNO_3NO_3^-$, $IN_2O_5^-$, and $IN_2O_7^-$ signals detected following irradiation of a mixture containing 0.5 M CAN and 1.0 M $NaNO_3$ (see Fig. 7).
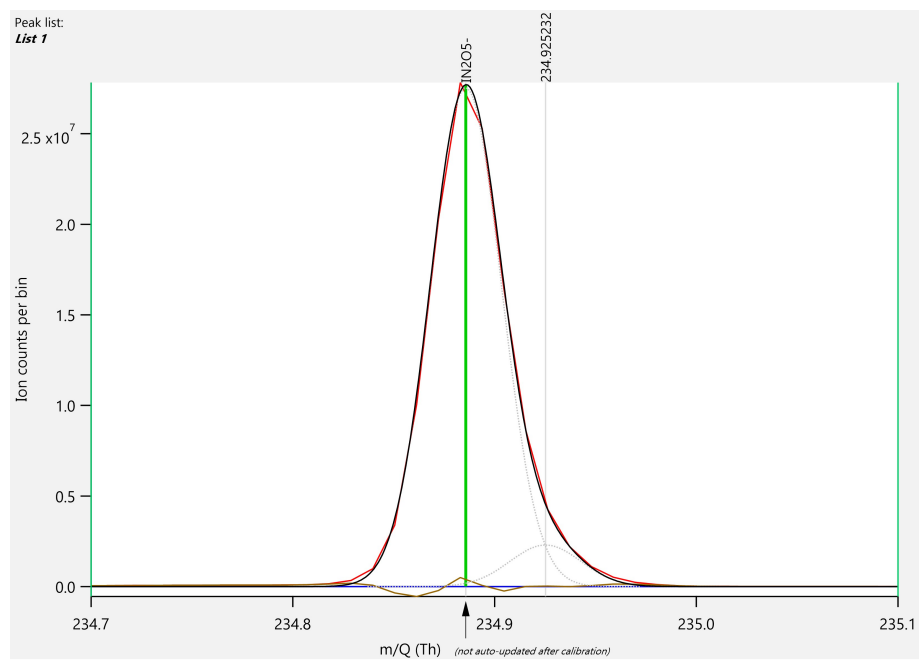
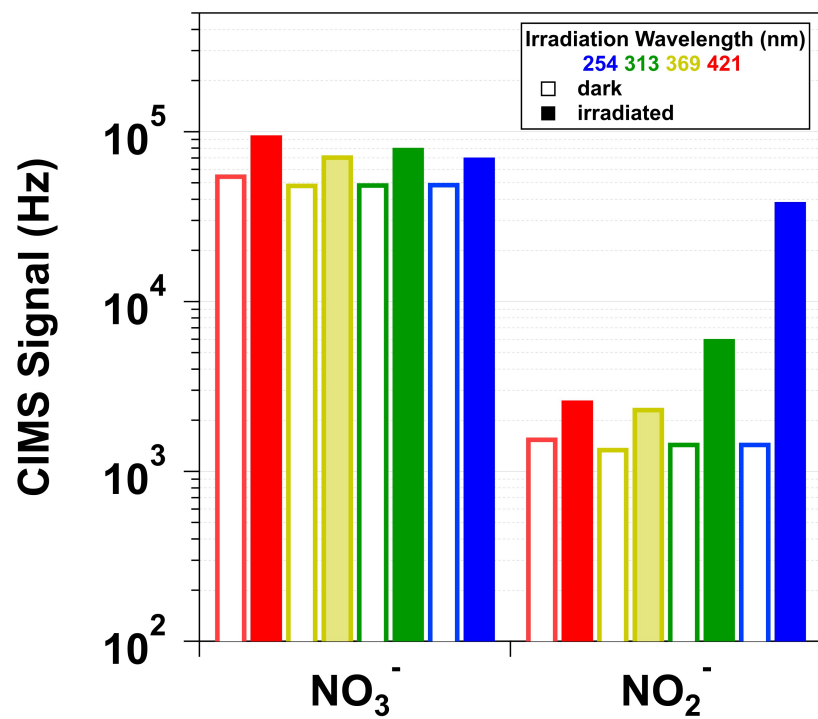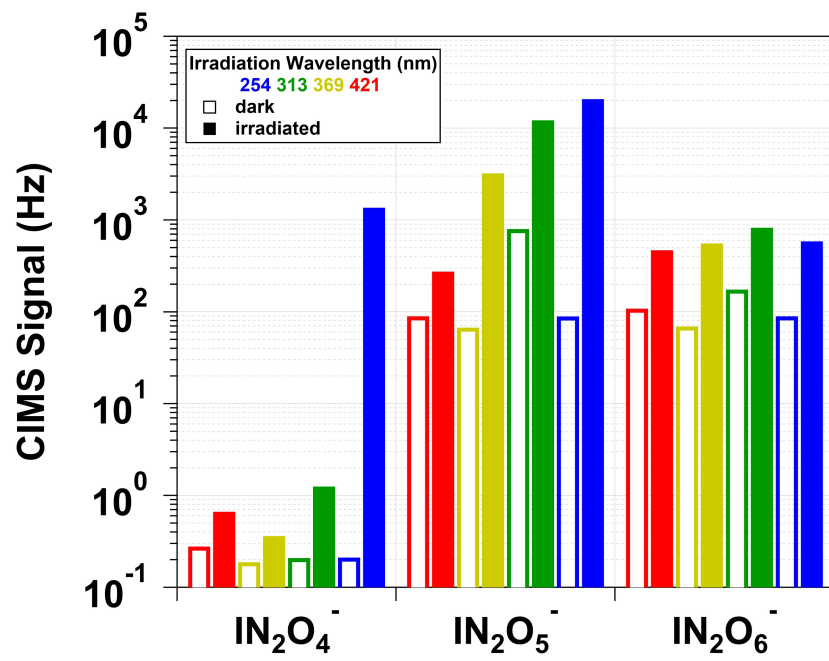**Figure S6.** HR-ToF-CIMS spectrum of m/Q=235 obtained following irradiation of CAN/HNO$_3$ mixtures.
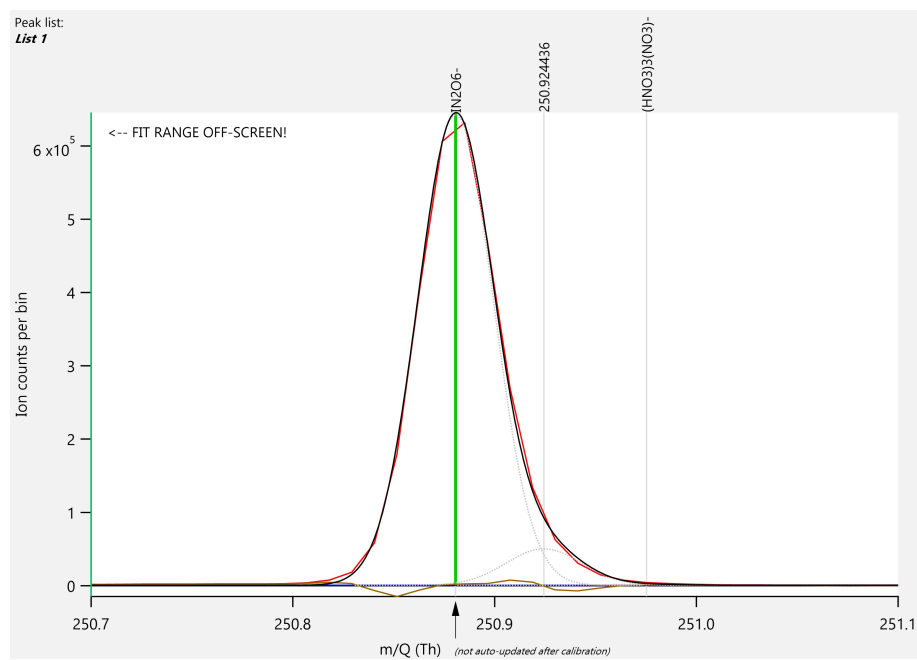
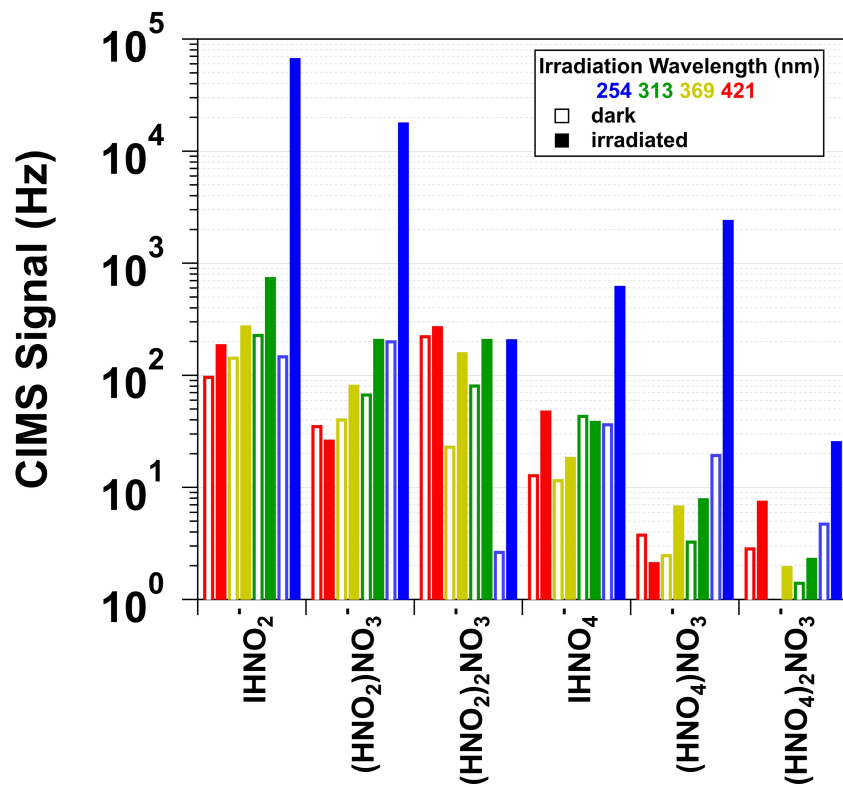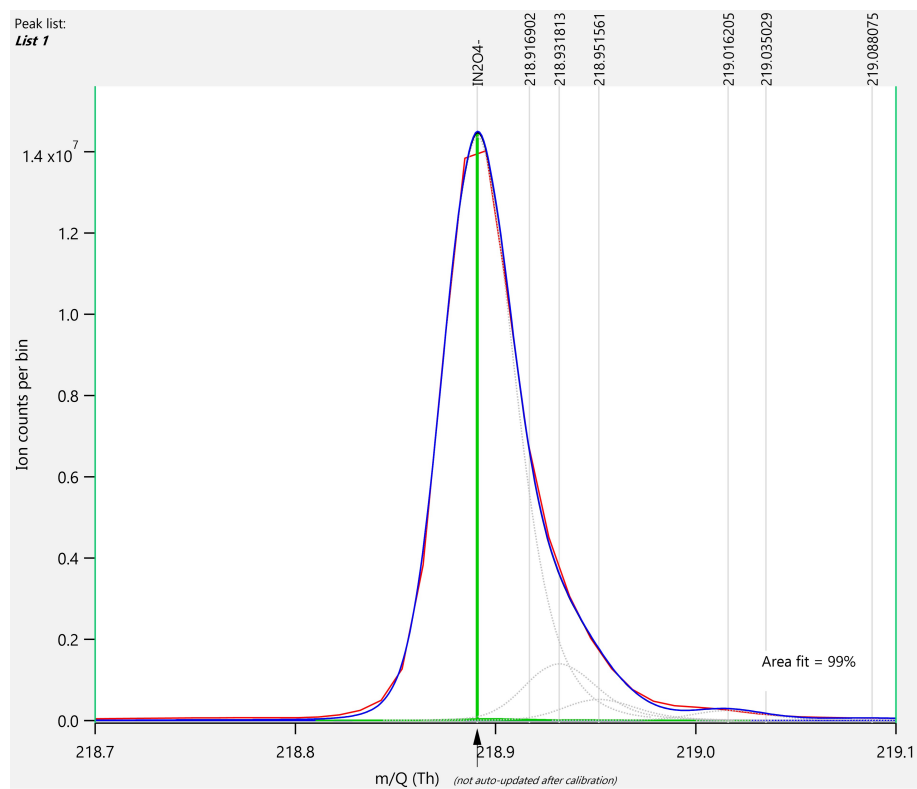**Figure S7.** HR-ToF-CIMS spectrum of m/Q=251 obtained following irradiation of CAN/HNO$_3$ mixtures.
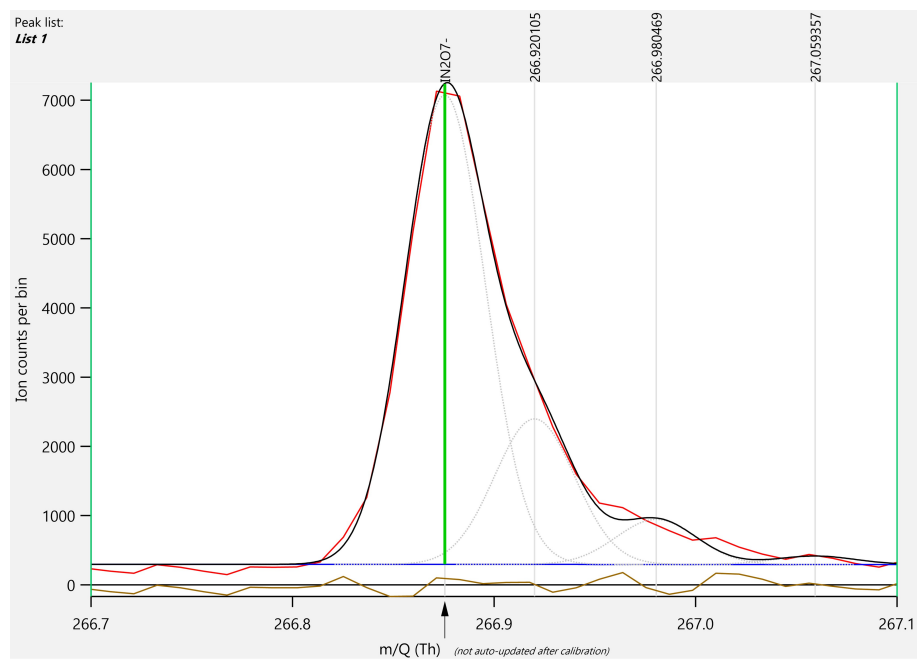
Figure S8. HR-ToF-CIMS spectrum of m/Q=267 obtained following irradiation of CAN/HNO$_3$ mixtures.

Figure S9. HR-ToF-CIMS NO_2^- and NO_3^- signals obtained during sampling of dark and irradiated neat CAN samples.
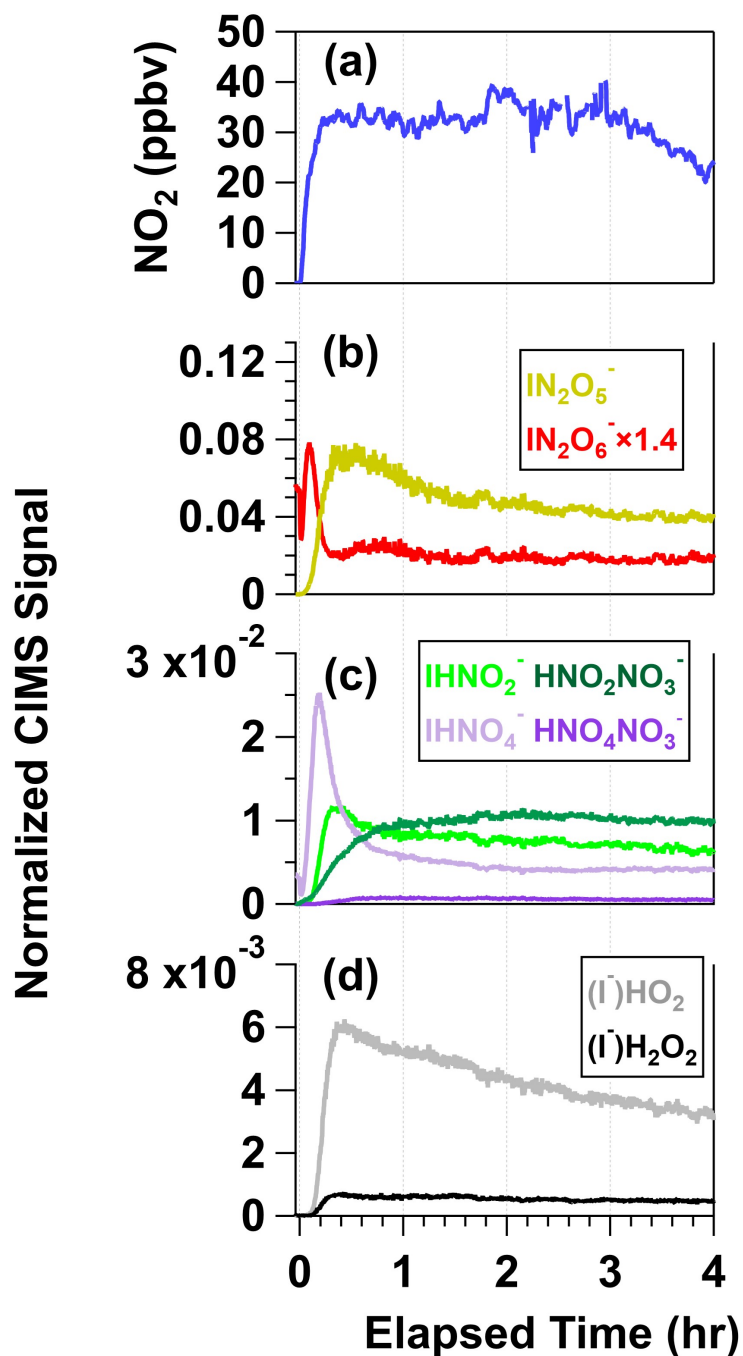
Figure S10. HR-ToF-CIMS $IN_2O_4^-$, $IN_2O_5^-$, and $IN_2O_6^-$ signals obtained during sampling of dark and irradiated neat CAN samples.

Figure S11. HR-ToF-CIMS $I(HNO_2)_n^-$, $(HNO_2)_nNO_3^-$, $I(HNO_4)_n^-$, and $(HNO_4)_nNO_3^-$ signals obtained during sampling of dark and irradiated neat CAN samples.

Figure S12. HR-ToF-CIMS spectrum of m/Q=219 obtained following irradiation of neat CAN samples.

Figure S13. Time series of **(a)** NO_2, **(b)** N_2O_5 and N_2O_6, **(c)** HNO_2 and HNO_4, and **(d)** HO_2 and H_2O_2 measured with NO_x analyzer and HR-ToF-CIMS during irradiation of a mixture containing 0.5 M CAN and 3.0 M HNO_3. N_2O_5, N_2O_6, HO_2 and H_2O_2 were detected as I^- adducts, and HNO_2 and HNO_4 were detected as both I^- and NO_3^- adducts.

Table S1. VOC tracers used in CAN/HNO$_3$ and CAN/NaNO$_3$ irradiation studies. Bimolecular rate coefficients for reaction with NO$_3$ are given in units of cm^3 molecule^{-1} s^{-1}.
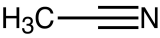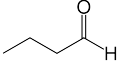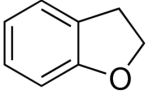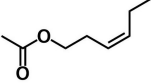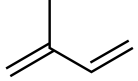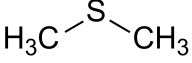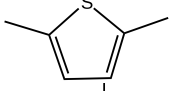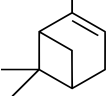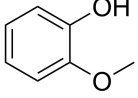
Compound	Formula	Structure	Mixing Ratio (ppb)	k$_{NO_3}$	References
Acetonitrile	C$_2$H$_3$N		517	$<3.01\times10^{-19}$	Cantrell et al. (1987)
Butanal	C$_4$H$_8$O		42	1.22×10^{-14}	D'Anna et al. (2001)
Thiophene	C$_4$H$_4$S		48	3.94×10^{-14}	Atkinson (1991)
2,3-Dihydrobenzofuran	C$_8$H$_8$O		34	1.15×10^{-13}	Atkinson (1991)
cis-3-Hexenyl-1-Acetate	C$_8$H$_{14}$O$_2$		24	2.46×10^{-13}	Atkinson et al. (1995)
Isoprene	C$_5$H$_8$		38	6.77×10^{-13}	Atkinson (1991)
Dimethyl Sulfide	C$_2$H$_6$S		6.5	1.09×10^{-12}	Atkinson et al. (2004)
2,5-Dimethylthiophene	C$_6$H$_8$S		4.2	2.52×10^{-12}	Cabañas et al. (2006)
α-Pinene	C$_{10}$H$_{16}$		3.0	6.16×10^{-12}	Atkinson (1991)
Guaiacol	C$_7$H$_8$O$_2$		2.1	2.69×10^{-11}	Lauraguais et al. (2016)

Table S2: KinSim mechanism used to calculate concentrations of species associated with irradiation of CAN/HNO$_3$ mixtures. Rate coefficients (blue text, red text or **black text**) or absorption cross sections (teal text) are given in units of cm^3 molecules^{-1} s^{-1} (blue text), M^{-1} s^{-1} (red text), cm^2 (teal text), or s^{-1} (**black text**). Condensed-phase reaction rate coefficients were used where possible, and otherwise were obtained from gas-phase reaction rate coefficients. Reaction rate coefficients in parentheses were obtained by applying a 6.022E+020 conversion factor to the other reaction coefficient listed in the same row. Citations of rate coefficient and absorption cross section values that are specifically applicable to mixtures containing [HNO$_3$] = 1.0 M, 3.0 M or 6.0 M are colored with brown, violet, or orange text, respectively.

Reactant 1	Reactant 2	Product 1	Product 2	Product 3	RateCoeff	Citation
Ce^{IV}NO$_3^-$	hν_{254}	[Ce^{III}...NO$_3$]*	NO$_3$		2.7E-17	**this work**
					3.1E-17	**this work**
					3.1E-17	**this work**
Ce^{IV}NO$_3^-$	hν_{313}	[Ce^{III}...NO$_3$]*	NO$_3$		3.1E-17	**this work**
					3.5E-17	**this work**
					4.5E-17	**this work**
Ce^{IV}NO$_3^-$	hν_{369}	[Ce^{III}...NO$_3$]*	NO$_3$		8.7E-18	**this work**
					1.2E-17	**this work**
					2.5E-17	**this work**
Ce^{IV}NO$_3^-$	hν_{421}	[Ce^{III}...NO$_3$]*	NO$_3$		1.0E-18	**this work**
					1.5E-18	**this work**
					4.4E-18	**this work**
[Ce^{III}...NO$_3$]*		Ce^{IV}NO$_3^-$			5.12E+04	**Martin and Stevens (1978)**
					6.30E+03	**Martin and Stevens (1978)**
					0	**Martin and Stevens (1978)**
[Ce^{III}...NO$_3$]*		Ce^{III}	NO$_3$		4.36E+04	**Martin and Stevens (1978)**
					6.76E+04	**Martin and Stevens (1978)**
					7.74E+04	**Martin and Stevens (1978)**
Ce^{III}	NO$_3$	Ce^{IV}NO$_3^-$			6.00E+07 (9.96E-14)	**Martin and Stevens (1978)**
					1.08E+06 (1.79E-15)	**Martin and Stevens (1978)**
					1.78E+06 (2.96E-15)	**Martin and Stevens (1978)**
NO$_3$	hν_{254}	NO$_2$	O		1.20E-19	Sander (1986)
NO$_3$	hν_{313}	NO$_2$	O		N/A	N/A
NO$_3$	hν_{369}	NO$_2$	O		9.56E-19	Schott and Davidson (1958)
NO$_3$	hν_{421}	NO$_2$	O		8.00E-20	Wayne et al. (1991)
NO$_3$	H$_2$O	H$^+$	NO$_3^-$	OH	5.30E+05 (8.80E-16)	Jiang et al. (1992)

Reactant 1	Reactant 2	Product 1	Product 2	Product 3	RateCoeff	Citation
NO_3	NO	$2\ NO_2$			(1.57E+10) 2.6E-11	Atkinson et al. (2004)
NO_3	NO_2	N_2O_5			1.70E+09 (2.82E-12)	Katsumura et al. (1991)
NO_3	NO_2^-	NO_3^-	NO_2		1.2E+09 (2.0E-12)	Daniels (1969)
NO_3	NO_3	N_2O_6			9.2E+05 (1.53E-15)	Martin and Stevens (1978)
NO_3	H	NO_2	OH		(5.66E+10) 9.4E-11	Becker et al. (1992)
NO_3	O	NO_2	O_2		(6.02E+09) 1.0E-11	DeMore et al. (1994)
NO_3	OH	NO_2	HO_2		(1.20E+10) 2.0E-11	Atkinson et al. (1994)
NO_3	HO_2	H^+	NO_3^-	O_2	3E+09 (4.98E-12)	Jiang et al. (1992)
NO_3	H_2O_2	H^+	NO_3^-	HO_2	7.1E+06 (1.7E-14)	Herrmann et al. (1994)
NO_3	HNO_2	H^+	NO_3^-	NO_2	8.0E+06 (1.3E-14)	Katsumura et al. (1991)
NO_2	$h\nu_{254}$	NO	O		1.1E-20	Sander et al. (2011)
NO_2	$h\nu_{313}$	NO	O		2.2E-19	Sander et al. (2011)
NO_2	$h\nu_{369}$	NO	O		5.6E-19	Sander et al. (2011)
NO_2	NO	N_2O_3			1.1E+09 (1.8E-12)	Grätzel et al. (1970)
NO_2	NO_2	N_2O_4			4.7E+08 (7.8E-13)	Poskrebyshev et al. (2001)
NO_2	O	NO	O_2		(6.02E+09) 1.0E-11	Atkinson et al. (2004)
NO_2	O	NO_3			(1.39E+10) 2.3E-11	Atkinson et al. (2004)
NO_2	H	HNO_2			1E+10 (1.7E-11)	Loegager and Sehested (1993)
NO_2	OH	H^+	NO_3^-		4.5E+09 (2.0E-11)	Loegager and Sehested (1993)
NO_2	HO_2	HNO_4			1.8E+09 (3.0E-12)	Loegager and Sehested (1993)
NO	O	NO_2			(1.81E+10) 3.0E-11	Atkinson et al. (2004)
NO	OH	HNO_2			2E+10 (3.3E-11)	Strehlow and Wagner (1982)
NO	HO_2	H^+	NO_3^-		3.2E+09 (5.3E-12)	Goldstein and Czapski (1995)
N_2O_3	$h\nu_{313}$	NO	NO_2		9.4E-19	Stockwell and Calvert (1978)
N_2O_3	$h\nu_{369}$	NO	NO_2		2.7E-19	Stockwell and Calvert (1978)
N_2O_3		NO	NO_2		3.6E+08	Atkinson et al. (2004)
N_2O_3	H_2O	$2\ HNO_2$			2.0E+08 (3.3E-13)	Park and Lee (1988)
N_2O_4	$h\nu_{254}$	$2\ NO_2$			6.5E-19	Sander et al. (2011)
N_2O_4	$h\nu_{313}$	$2\ NO_2$			2.5E-19	Sander et al. (2011)
N_2O_4	$h\nu_{369}$	$2\ NO_2$			1.3E-19	Sander et al. (2011)
N_2O_4		$2\ NO_2$			6800	Poskrebyshev et al. (2001)
N_2O_4	H_2O	H^+	NO_3^-	HNO_2	1.5E+08 (2.49E-13)	Park and Lee (1988)
N_2O_5	$h\nu_{254}$	NO_2	NO_3		3.2E-19	Sander et al. (2011)

Reactant 1	Reactant 2	Product 1	Product 2	Product 3	RateCoeff	Citation
N_2O_5	$h\nu_{313}$	NO_2	NO_3		1.6E-20	Sander et al. (2011)
N_2O_5	$h\nu_{369}$	NO_2	NO_3		7.2E-22	Sander et al. (2011)
N_2O_5	$h\nu_{421}$	NO_2	NO_3		8.0E-23	Sander et al. (2011)
N_2O_5		NO_2	NO_3		0.06	Atkinson et al. (2004)
N_2O_5	H_2O	$2 H^+$	$2 NO_3^-$		(7.8) 1.3E-20	Morris and Niki (1973)
HNO_2	$h\nu_{254}$	NO	OH		1.4E-19	Sander et al. (2011)
HNO_2	$h\nu_{313}$	NO	OH		2.2E-20	Sander et al. (2011)
HNO_2	$h\nu_{369}$	NO	OH		3.1E-19	Sander et al. (2011)
HNO_2	$h\nu_{421}$	NO	OH		2.4E-21	Sander et al. (2011)
HNO_2	H	NO	H_2O		4.5E+08 (7.5E-13)	Halpern and Rabani (1966)
HNO_2	OH	NO_2	H_2O		(3.61E+09) 6.0E-12	Atkinson et al. (2004)
HNO_3	$h\nu_{254}$	NO_2	OH		2.0E-20	Sander et al. (2011)
HNO_3	$h\nu_{313}$	NO_2	OH		6.3E-22	Sander et al. (2011)
HNO_3	$h\nu_{369}$	NO_2	OH		4.2E-24	Sander et al. (2011)
HNO_3	OH	NO_3	H_2O		5.3E+07 (8.8E-14)	Jiang et al. (1992)
HNO_4	$h\nu_{254}$	NO_2	HO_2		3.5E-19	Sander et al. (2011)
HNO_4	$h\nu_{313}$	NO_2	HO_2		4.7E-21	Sander et al. (2011)
HNO_4	$h\nu_{369}$	NO_2	HO_2		1.7E-22	Sander et al. (2011)
HNO_4		NO_2	HO_2		4.6E-03	Lammel et al. (1990)
HNO_4		HNO_2	O_2		7E-04	Loegager and Sehested (1993)
HNO_4	OH				(2.83E+09) 4.70E-12	Atkinson et al. (2004)
H	O_2	HO_2			1.0E+10 (1.7E-11)	Elliot et al. (1990)
H	O_2	H_2O_2			2.0E+10 (3.3E-11)	Feng et al. (1970)
OH	O	O_2	H		(2.0E+10) 3.3E-11	DeMore et al. (1997)
OH	OH	H_2O_2			4.2E+09 (7.0E-12)	Elliot et al. (1990)
OH	HO_2	O_2	H_2O		1.0E+10 (1.7E-11)	Elliot and Buxton (1992)
OH	HO_2	H_2O_3			(2.14E+09) 3.55E-12	Badenes et al. (2017)
OH	H_2O_2	HO_2	H_2O		(1.0E+09) 1.7E-12	Atkinson et al. (2004)
H_2O_2	$h\nu_{254}$	2OH			6.7E-20	Sander et al. (2011)
H_2O_2	$h\nu_{313}$	2OH			3.4E-21	Sander et al. (2011)
H_2O_2	$h\nu_{369}$	2OH			7.2E-23	Kahan et al. (2012)
H_2O_2	$h\nu_{421}$	2OH			9.2E-24	Kahan et al. (2012)
H_2O_2	H	H_2O	OH		3.6E+07 (6.0E-14)	Mezyk and Bartels (1995)

Reactant 1	Reactant 2	Product 1	Product 2	Product 3	RateCoeff	Citation
H_2O_2	O	HO_2	OH		1.6E+09 (2.7E-12)	Sauer et al. (1984)
NO_3^-	H	H_2O	NO_2		1.0E+07 (1.7E-14)	Jiang et al. (1992)
NO_3^-	H^+	HNO_3			6.0E+08 (1.0E-12)	Poskrebyshev et al. (2001)

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Table S3. Room-temperature bimolecular rate coefficients (k_{298}) used to calculate fates of alkyl and acyl organic peroxy radicals (alkyl-RO_2, acyl-RO_2) formed from VOC + NO_3 reactions as a function of CAN irradiation conditions summarized in Fig. 6. Kinetic data is adapted from Orlando and Tyndall (2012). Rate coefficients are given in units of cm^3 $molecule^{-1}$ s^{-1}.

Reactant 1	Reactant 2	k_{298}
alkyl-RO_2	HO_2	7.7×10^{-12}
acyl-RO_2	HO_2	1.4×10^{-11}
alkyl-RO_2	NO_3	2.4×10^{-12}
acyl-RO_2	NO_3	3.2×10^{-12}
acyl-RO_2	NO_2	1.1×10^{-11}

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