

Supporting information

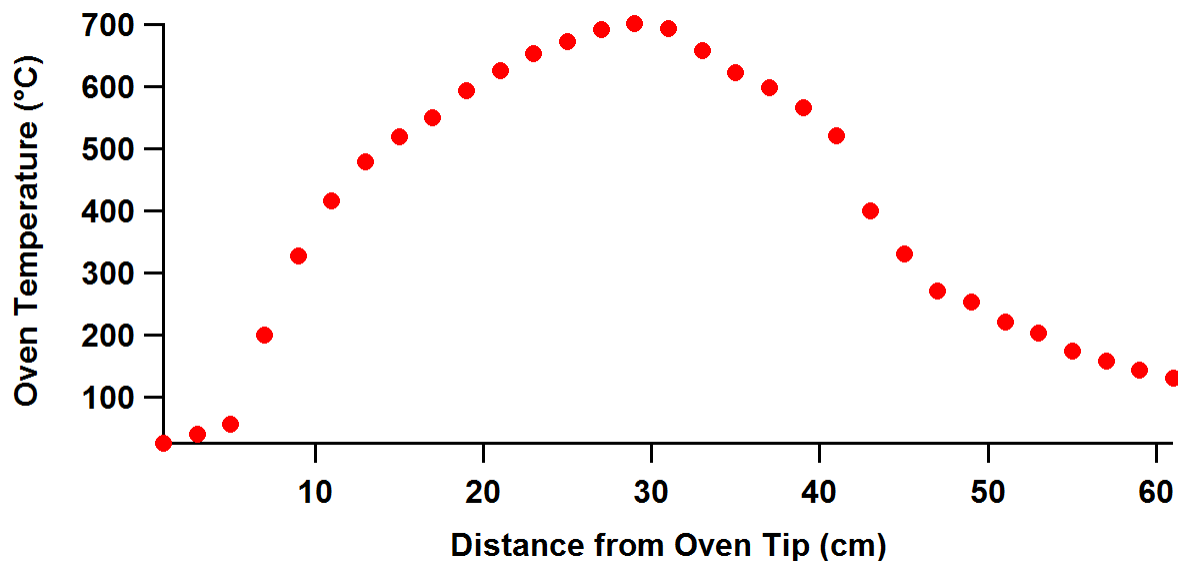


Figure S1. A sample oven temperature profile measured with a 2.0 slpm flow rate through the TD oven inlet, while the oven was set at 650 °C. Distance is measured from end of the quartz tube. The first ~5 cm are not heated, and the heated portion stretched from approximately 5 – 42 cm, with a cool down region from 42 – 63 cm.

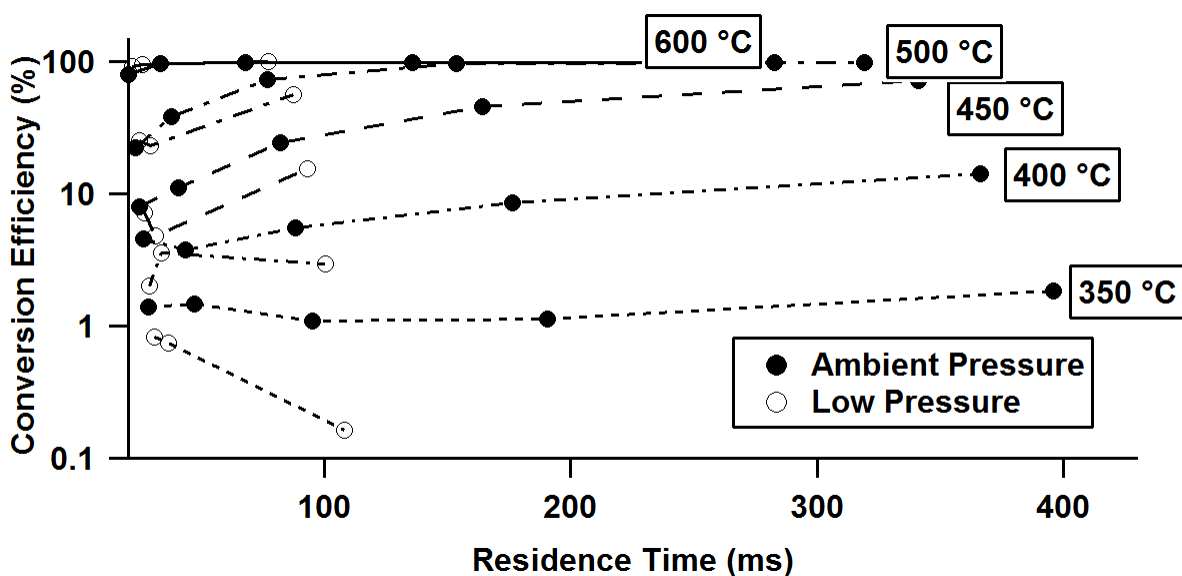


Figure S2. Log scale plot of conversion efficiency vs residence time. This plot is similar to the linear plot in Fig. 3, but is presented in log space to highlight small differences in the low conversion efficiency region.

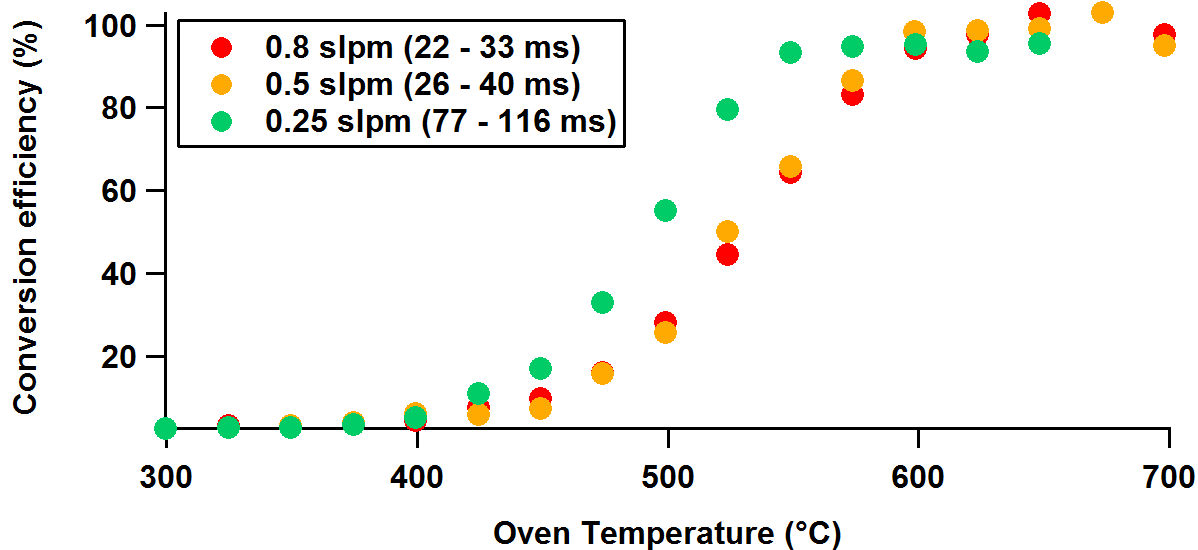


Figure S3. HNO₃ thermograms taken at low oven pressure (~250 mbar). As in Fig. 2, the onset of signal shifts to higher temperatures at faster flow rates.

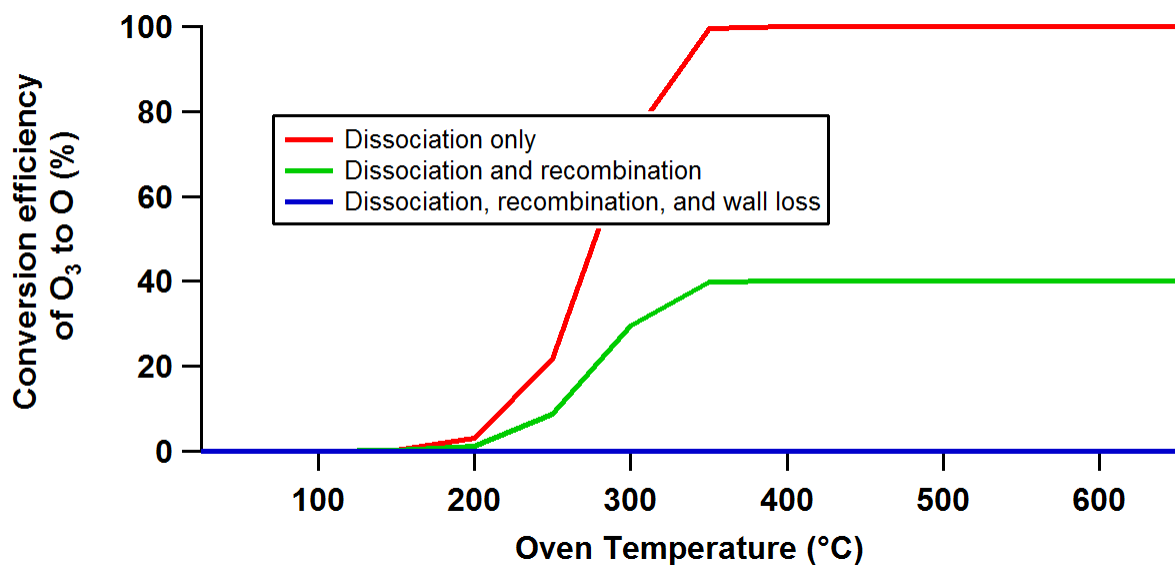


Figure S4. A simulated O₃ dissociation curve to O. These results indicate that O₃ dissociates to form O at the entire temperature range relevant for AN and HNO₃ TD ovens, but that if allowed to recombine, only ~40% will be allowed to recombine, but that nearly all O atoms could be lost to reactions with the wall.

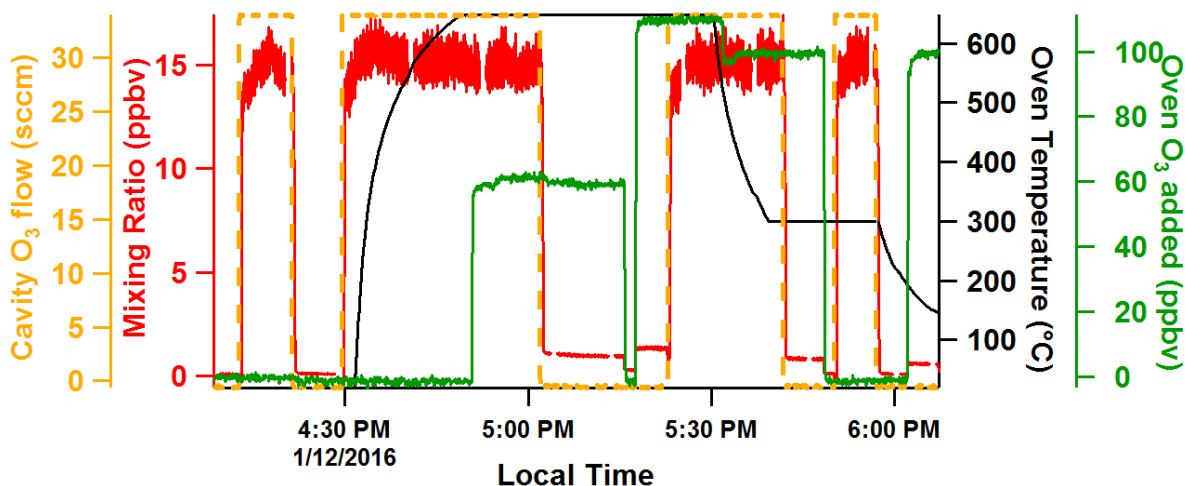


Figure S5. The measured NO_2 mixing ratios as ~ 15 ppbv NO in zero air is introduced to the NO_y thermal dissociation inlet is shown in red. The green and yellow lines represent the addition of O_3 in two places: ppbv levels before the NO sample enters the TD inlet (green) and ppmv levels in the mixing volume just prior to entering the CRDS cavity (yellow). The mixing volume O_3 converts any NO to NO_2 prior to detection, so when this O_3 is added (such as between 4:30 and 5pm), the measured NO_2 is ~ 15 ppbv, as expected. When O_3 is not added to either the TD inlet or the mixing volume (such as between 4:20 and 4:30pm), no NO_2 signal is observed. However, when O_3 is added to the TD inlet, but not to the mixing volume, and the oven is at 650°C , (such as between 5:05 and 5:15), approximately 2.25 ppbv NO_2 is observed, indicating that this NO_2 is formed by reaction of O_3 and NO in the oven. This has no effect on this TD-CRDS instrument, as any NO would be converted to NO_2 in the mixing volume region immediately following the TD oven. But techniques such as TD-LIF or TD-CRDS in which NO is not converted to NO_2 would see a $\sim 15\%$ conversion of ambient NO to NO_2 , which must be accounted for.

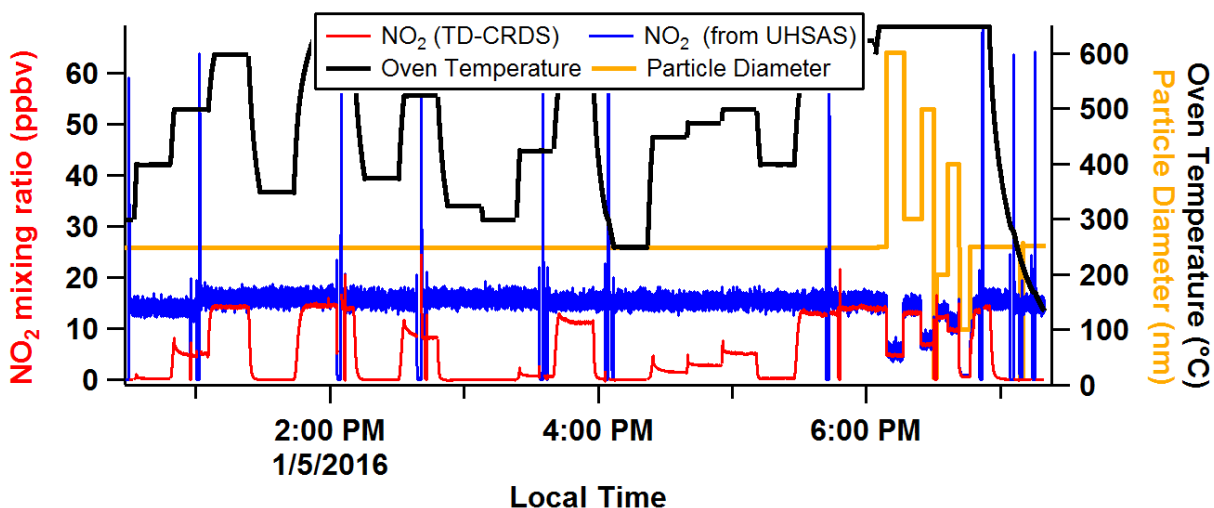


Figure S6. NO_2 signal (red) detected in the NO_y channel of the TD-CRDS instrument when NH_4NO_3 aerosol is introduced to the inlets on two separate occasions. The blue trace is the expected NH_4NO_3 concentrations derived from the UHSAS measurement of the particle size distribution. The yellow indicates set DMA diameter.

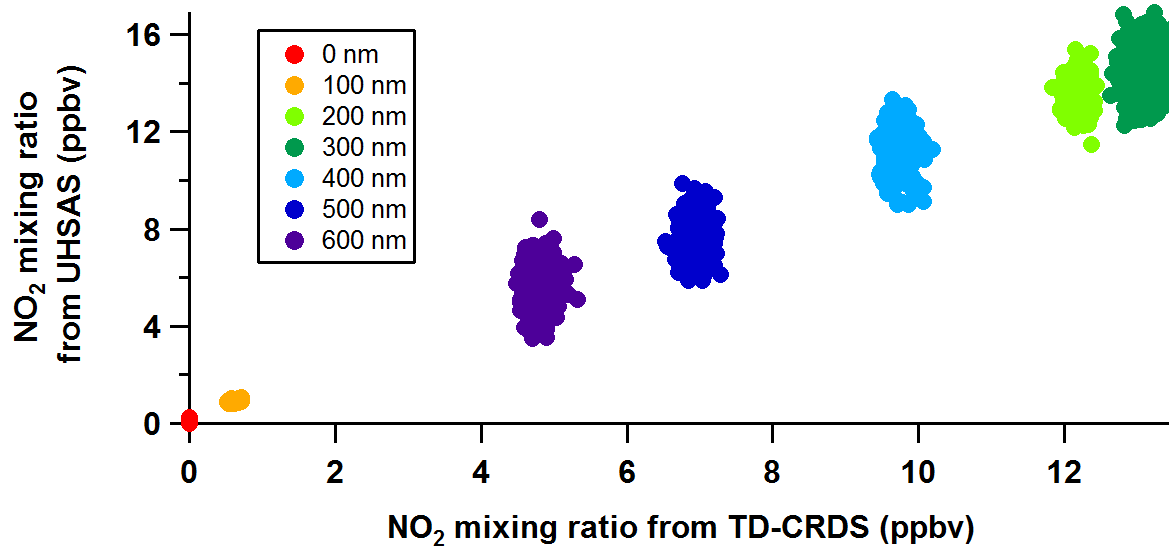


Figure S7. NO₂ mixing ratios as measured by the TD-CRDS instrument, and derived NO₂ mixing ratios from the UHSAS size distribution of NH₄NO₃ particles, colored by DMA selected size. A linear trend is shown in the scatter plot, with no dependence on particle size, emphasizing that complete conversion of the NH₄NO₃ particles is observed in the TD oven.

Table S1. Reactions used in HNO₃ box model

Rate laws are presented in table form, where the parameters listed can be inserted into the equation $k(T) = A(298/T)^{n_0}e^{-(E_a/RT)}$. For third order equations, a high pressure limit is also given. All rates taken from the JPL (<http://jpldataeval.jpl.nasa.gov/>), IUPAC (<http://iupac.pole-ether.fr/>), or NIST (<http://kinetics.nist.gov/kinetics/index.jsp>) databases. For reactions from the NIST database, the individual study is referenced.

Reaction	Rate Law						Reference
	A ₀	n ₀	E _a /R ₀	A _∞	n _∞	E _a /R _∞	
HNO ₃ → NO ₂ + OH	1.83e-4	-1.98	24054	1.26e-15	0	24054	NIST 1974GLA
NO ₃ → NO ₂ + O	*See main text*						
NO ₃ + NO ₂ → N ₂ O ₅	2.0e-30	-4.4	0	1.4e-12	-0.7	0	JPL
NO ₂ + O → NO ₃	2.50e-31	-1.8	0	2.2e-11	-0.7	0	JPL
NO ₂ + OH → HNO ₃	1.80e-30	-3	0	2.80e-11	0	0	JPL
NO ₂ + HO ₂ → HO ₂ NO ₂	2.00e-31	-3.4	0	2.90e-12	-1.1	0	JPL
NO + O → NO ₂	9.00e-32	-1.5	0	3.00e-11	0	0	JPL
NO + OH → HONO	7.00e-31	-2.6	0	3.60e-11	-0.1	0	JPL
NO + H → HNO	1.22e-31	-1.17	211.6	N/A	N/A	N/A	JPL
O ₃ → O + O ₂	7.16e-10	0	11200	N/A	N/A	N/A	NIST 1979HEI
O ₂ + H → HO ₂	4.40e-32	-1.3	0	7.50e-11	0.2	0	JPL
O + H → OH	4.36e-32	-1	0	N/A	N/A	N/A	NIST 1986TSA
2OH → H ₂ O ₂	6.90e-31	-1	0	2.60e-11	0	0	JPL
OH + H → H ₂ O	4.38e-30	-2	0	N/A	N/A	N/A	NIST 1992BAU
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	3.00e-13	0	-460				JPL
N ₂ O ₃ → NO + NO ₂	1.90e-7	-8.7	4800	4.7e15	0.4	4880	IUPAC
HO ₂ NO ₂ → HO ₂ + NO ₂	4.10e-5	0	10650	4.8e15	0	11170	IUPAC
HONO → OH + NO	1.98e-3	-3.8	25257	1.09e16	-1.23	25016	NIST 1991TSA
HNO → NO + H	5.48e-7	-1.24	25257	N/A	N/A	N/A	NIST 1991TSA
H ₂ O ₂ → 2OH	2.03e-3	-4.86	26820	N/A	N/A	N/A	NIST 1986TSA
N ₂ O ₅ → NO ₂ + NO ₃	1.30e-3	-3.5	11000	9.7e14	0.1	11080	IUPAC
HNO ₃ + OH → H ₂ O + NO ₃	6.50e-34	0	-1335	2.70e-17	0	-2199	JPL**
2NO ₃ → 2NO ₂ + O ₂	8.5e-13	0	2450				JPL
NO ₃ + NO → 2NO ₂	1.79e-11	0	-109.45				NIST 1992ATK
NO ₃ + O → O ₂ + NO ₂	1.00e-17	0	0				JPL
NO ₃ + OH → HO ₂ + NO ₂	2.2e-11	0	0				JPL
NO ₃ + HO ₂ → O ₂ + HNO ₃	3.5e-12	0	0				JPL
NO ₃ + H → NO ₂ + OH	9.4e-11	0	0				NIST 1992BEC
NO ₂ + O ₃ → NO ₃ + O ₂	1.2e-13	0	2450				JPL
NO ₂ + O → NO + O ₂	5.10e-12	0	-210				JPL
NO ₂ + HNO → HONO + NO	1e-12	0	1000				NIST 1991TSA
NO ₂ + H → NO + OH	4.00e-10	0	340				JPL
NO + O ₃ → NO ₂ + O ₂	3.00e-12	0	1500				JPL
NO + HO ₂ → NO ₂ + OH	3.30e-12	0	-270				JPL
O ₃ + O → 2O ₂	8.00e-12	0	2060				JPL
O ₃ + OH → HO ₂ + O ₂	1.70e-12	0	940				JPL
O ₃ + HNO → HONO + O ₂	2.56e-15	3.59	-396.9				NIST 2007XU
O ₃ + H → O ₂ + OH	1.40e-10	0	470.26				NIST 1997DEM
O ₂ + H → OH + O	1.22e-11	0.96	6157.9				NIST 2012TUR

$O + OH \rightarrow O_2 + H$	1.80e-11	0	-180	2.18e-11			JPL
$O + HO_2 \rightarrow OH + O_2$	3.00e-11	0	-200				JPL
$O + N_2O_3 \rightarrow \text{Products}$	4.30e-13	0	0				NIST 1987GEE
$O + HO_2NO_2 \rightarrow \text{Products}$	7.8e-11	0	3400				JPL
$O + HONO \rightarrow OH + NO_2$	2.01e-11	0	3000				NIST 1991TSA
$O + HNO \rightarrow OH + NO$	6.00e-11	0	0				NIST 1991TSA
$O + H_2O_2 \rightarrow HO_2 + OH$	1.40e-12	0	2000				JPL
$2OH \rightarrow H_2O + O$	1.80e-12	0	0				JPL
$OH + HO_2 \rightarrow H_2O + O_2$	4.80e-11	0	-250				JPL
$OH + HO_2NO_2 \rightarrow H_2O_2 + NO_3$	1.30e-12	0	-380				JPL
$OH + HO_2NO_2 \rightarrow HO_2 + HNO_3$	1.30e-12	0	-380				JPL
$OH + HONO \rightarrow H_2O + NO_2$	1.80e-11	0	390				JPL
$OH + HNO \rightarrow H_2O + NO$	8.00e-11	0	500				NIST 1991TSA
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	2.90e-12	0	160				IUPAC
$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$	1.00e-13	0	0				NIST 1974VAR
$HO_2 + H \rightarrow H_2O + O$	5.00e-11	0	865.95				NIST 1992BAU
$HO_2 + H \rightarrow 2OH$	2.81e-10	0	440.19				NIST 1992BAU
$HO_2 + H \rightarrow O_2 + H_2$	7.11e-11	0	709.6				NIST 1992BAU
$HO_2NO_2 + H \rightarrow \text{Products}$	2.46e-14	0	0				NIST 1981TRE
$HONO + H \rightarrow H_2O + NO$	6.39e-13	1.89	1940				NIST 1997HSU
$HONO + H \rightarrow OH + HNO$	1.26e-11	0.86	2500				NIST 1997HSU
$HNO + H \rightarrow H_2 + NO$	3.01e-11	0	500				NIST 1991TSA
$H_2O_2 + H \rightarrow OH + H_2O$	1.69e-11	0	1800				NIST 1992BAU
$H_2O_2 + H \rightarrow H_2 + HO_2$	2.81e-12	0	1889.5				NIST 1992BAU
$OH \rightarrow \text{Wall}$				46 s ⁻¹			**See main text
$O \rightarrow \text{Wall}$				70 s ⁻¹			**See main text
$C_3H_8 + O \rightarrow C_3H_7 + OH$	1.37e-12	2.68	1870.2				NIST 1988TSA
$C_3H_8 + H \rightarrow C_3H_7 + H_2$	4.23e-12	2.54	3400				NIST 1988TSA
$C_3H_8 + NO_3 \rightarrow C_3H_7 + HNO_3$	4.17e-12	0	3260.6				NIST 2002BRA
$C_3H_8 + NO_2 \rightarrow C_3H_7 + HONO$	4.00e-13	0	11400				NIST 1976TIT
$C_3H_8 + O_3 \rightarrow \text{Products}$	2.74e-13	0	7270				NIST 1963MOR
$C_3H_8 + OH \rightarrow C_3H_7 + H_2O$	1.44e-12	1	130				NIST 1985WAL
$C_3H_7 + O \rightarrow \text{Products}$	1.37e-12	2.68	1870				NIST 1988TSA
$CO + O \rightarrow CO_2$	1.70e-33	0	1509	1e-14	0	1629	NIST 1986TSA

Reactions used in N₂O₅ box model

Reaction	Rate Law						Reference
	A ₀	n ₀	Ea/R ₀	A _∞	n _∞	Ea/R _∞	
$NO_3 + NO_2 \rightarrow N_2O_5$	2.0e-30	-4.4	0	1.4e-12	-0.7	0	JPL
$NO_2 + O \rightarrow NO_3$	2.50e-31	-1.8	0	2.2e-11	-0.7	0	JPL
$NO + O \rightarrow NO_2$	9.00e-32	-1.5	0	3.00e-11	0	0	JPL
$O_2 + O \rightarrow O_3$	6.00e-34	-2.4	0	0	0	0	JPL
$O + O \rightarrow O_2$	5.21e-35	0	-900				NIST 1986TSA
$N_2O_5 \rightarrow NO_2 + NO_3$	1.30e-3	-3.5	11000	9.7e14	0.1	11080	IUPAC
$NO_3 + NO \rightarrow 2NO_2$	1.79e-11	0	-109.45				NIST 1992ATK
$NO_3 + O \rightarrow O_2 + NO_2$	1.00e-17	0	0				JPL
$NO_2 + O \rightarrow NO + O_2$	5.10e-12	0	-210				JPL

$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	1.2e-13	0	2450				JPL
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	3.00e-12	0	1500				JPL
$\text{O}_3 \rightarrow \text{O} + \text{O}_2$	7.16e-10	0	11200	N/A	N/A	N/A	NIST 1979HEI
$\text{O} \rightarrow \text{Walls}$	70 s ⁻¹						*see main text*
$\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}$	*see main text*						

Reactions used in NH₃ box model

Reaction	Rate Law						Reference
	A ₀	n ₀	Ea/R ₀	A _∞	n _∞	Ea/R _∞	
$\text{HNO} \rightarrow \text{NO} + \text{H}$	5.48e-7	-1.24	25257	N/A	N/A	N/A	NIST 1991TSA
$\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$	2.87e-13	2.1	0				NIST 1991COH
$\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$	4.48e-13	1.8	0				NIST 1986JEF
$\text{NH}_2 + \text{O}_3 \rightarrow \text{NH}_2\text{O} + \text{O}_2$	4.9e-12	0	1000				NIST 2004ATK
$\text{NH}_2 + \text{O} \rightarrow \text{HNO} + \text{H}$	7.47e-11	0	0				NIST 1991COH
$\text{NH}_2 + \text{O} \rightarrow \text{OH} + \text{NH}$	1.16e-11	0	0				NIST 1991COH
$\text{NH}_2 + \text{O} \rightarrow \text{NO} + \text{H}_2$	8.30e-12	0	0				NIST 1991COH
$\text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_4$	1.96e-29	-3.9	0	N/A	N/A	N/A	NIST 1995FAG
$\text{NH}_2 + \text{OH} \rightarrow \text{NH}_2\text{OH}$	6.77e-10	-3.23	673				NIST 2009MOU
$\text{NH}_2 + \text{OH} \rightarrow \text{NH} + \text{H}_2\text{O}$	7.69e-13	1.5	-230				NIST 1991COH
$\text{NH}_2 + \text{OH} \rightarrow \text{NH}_3 + \text{O}$	4.95e-15	2.6	-870				NIST 1991COH
$\text{NH}_2 + \text{NH} \rightarrow \text{N}_2\text{H}_2 + \text{H}$	1.5e-10	-0.27	-38.4				NIST 2009KLI
$\text{NH}_2 + \text{NH}_2\text{OH} \rightarrow \text{NH}_3 + \text{NH}_2\text{O}$	1.42e-15	4	-13.03				NIST 2009KLI
$\text{NH}_2\text{O} + \text{O}_3 \rightarrow \text{Products}$	2.01e-14	0	0				NIST 1980BUL
$\text{NH}_2\text{O} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HNO}$	1.66e-12	0	0				NIST 1992LIN
$\text{NH}_2\text{OH} \rightarrow \text{OH} + \text{NH}_2$	0.16	-5.96	33555				NIST 2009KLI
$\text{NH} + \text{OH} \rightarrow \text{HNO} + \text{H}$	3.32e-11	0	0				NIST 1991COH
$\text{NH}_2\text{OH} + \text{NH} \rightarrow \text{NH}_2 + \text{NH}_2\text{O}$	3.73e-16	4.4	786.6				NIST 2009KLI
$\text{NO} + \text{O} \rightarrow \text{NO}_2$	9.00e-32	-1.5	0	3.00e-11	0	0	JPL
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	3.00e-12	0	1500				JPL
$\text{NO}_2 + \text{O} \rightarrow \text{NO}_3$	5.10e-12	0	-210				JPL
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	1.2e-13	0	2450				JPL
$\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}$	**See main text						
$\text{NO} + \text{H} \rightarrow \text{HNO}$	1.22e-31	-1.17	211.6	N/A	N/A	N/A	JPL
$\text{O}_3 \rightarrow \text{O} + \text{O}_2$	7.16e-10	0	11200	N/A	N/A	N/A	NIST 1979HEI
$\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{NO}_2$	1.79e-11	0	-109.45				NIST 1992ATK
$\text{NO}_3 + \text{O} \rightarrow \text{O}_2 + \text{NO}_2$	1.00e-17	0	0				JPL
$\text{NO}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{NO}_2$	2.2e-11	0	0				JPL
$\text{HNO} + \text{H} \rightarrow \text{NH}_2 + \text{O}$	1.05e-9	-0.3	14673				NIST 1991COH
$\text{HNO} + \text{H} \rightarrow \text{OH} + \text{NH}$	2.41e-9	-0.5	9009				NIST 1991COH
$\text{HNO} + \text{H} \rightarrow \text{H}_2 + \text{NO}$	3.01e-11	0	500				NIST 1991TSA
$\text{O} + \text{HNO} \rightarrow \text{OH} + \text{NO}$	6.00e-11	0	0				NIST 1991TSA
$\text{OH} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{NO}$	8.00e-11	0	500				NIST 1991TSA
$\text{O} \rightarrow \text{Walls}$	~70 s ⁻¹						**See main text
$\text{OH} \rightarrow \text{Walls}$	~46 s ⁻¹						**See main text