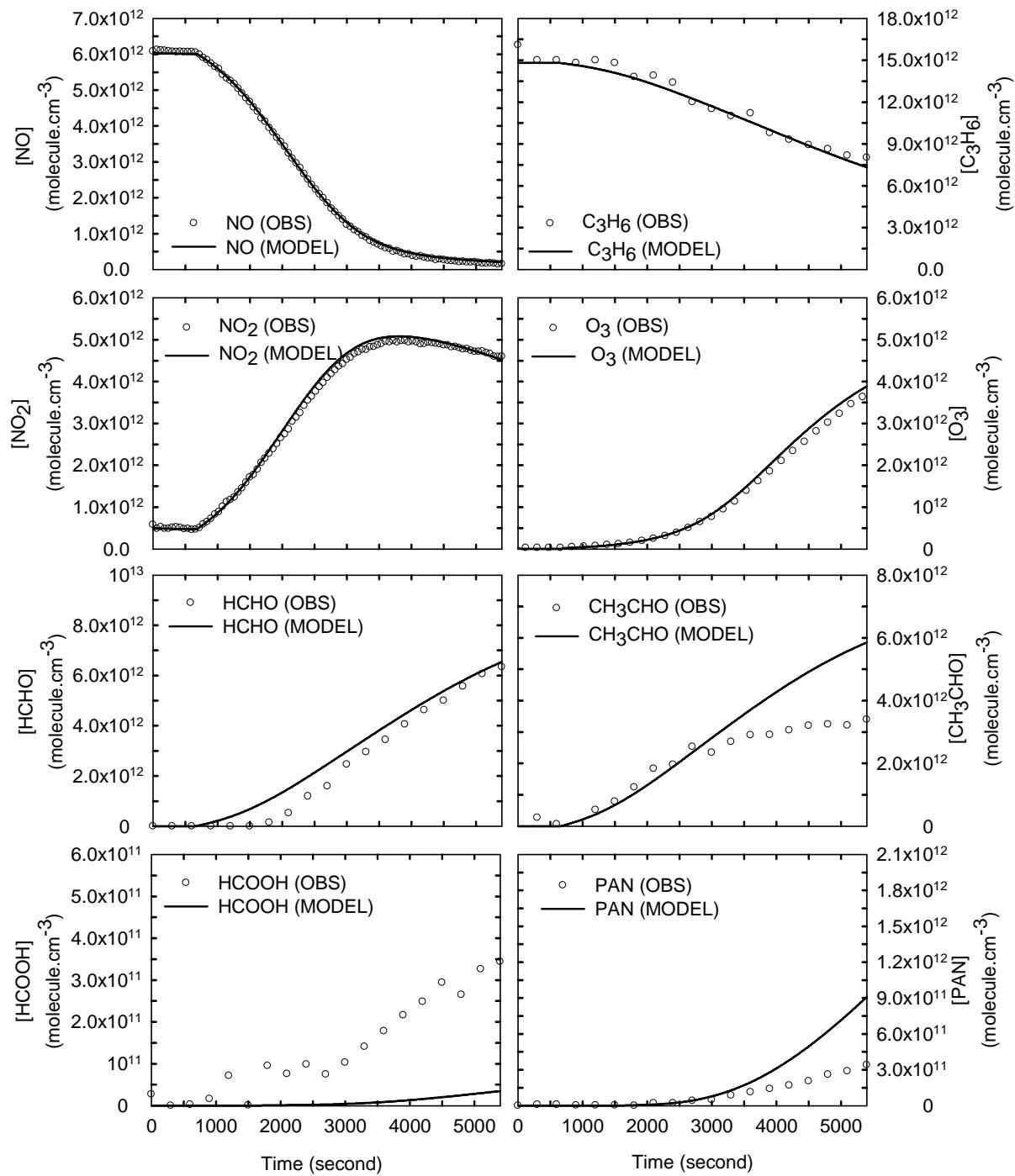


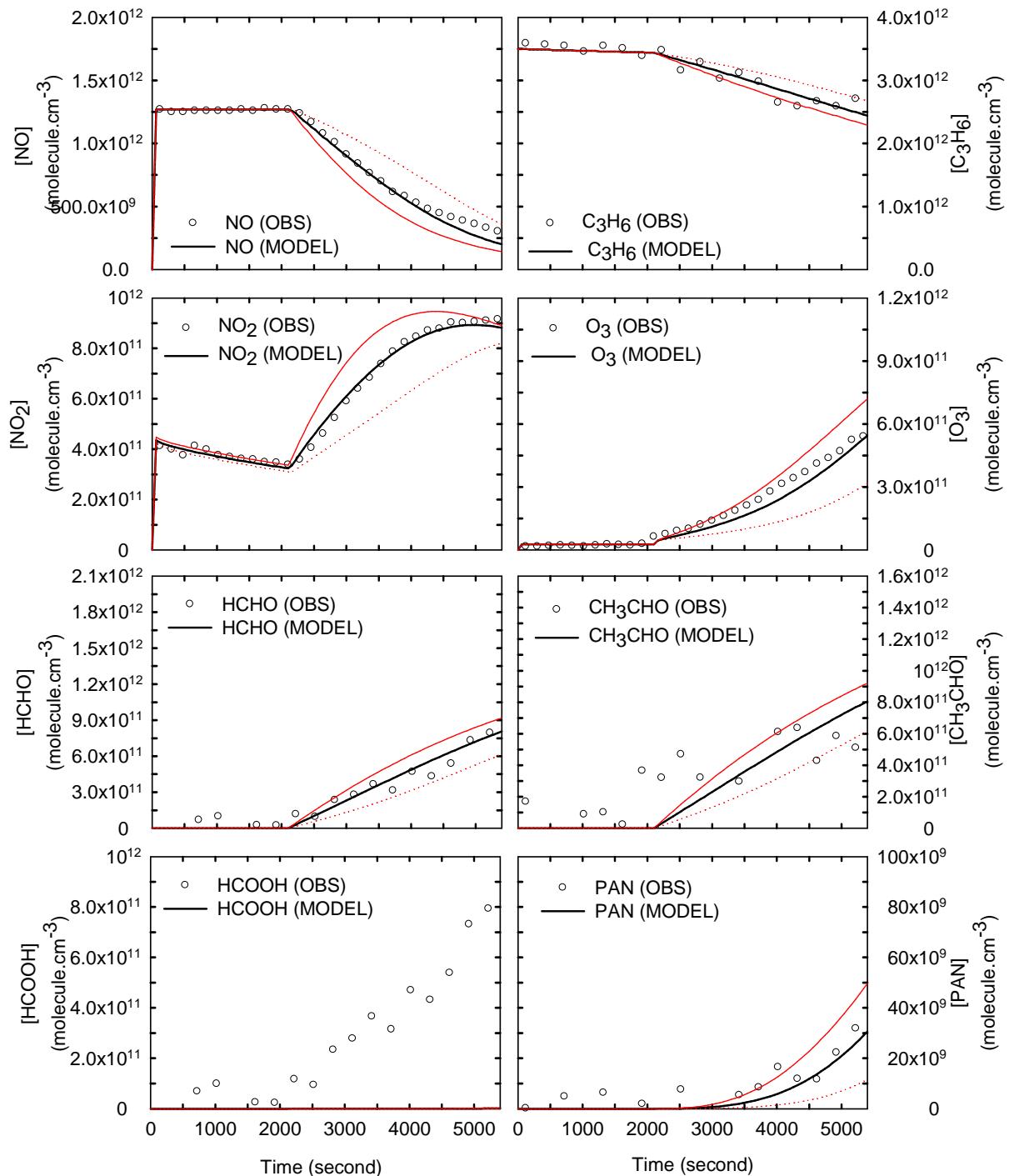
## SUPPLEMENTARY MATERIAL

Chemical reaction system used for the modelling of NOx-Air experiments. Rate constants are taken from Atkinson et al., 2004, Atkinson et al., 2006, Atkinson et al., 2007

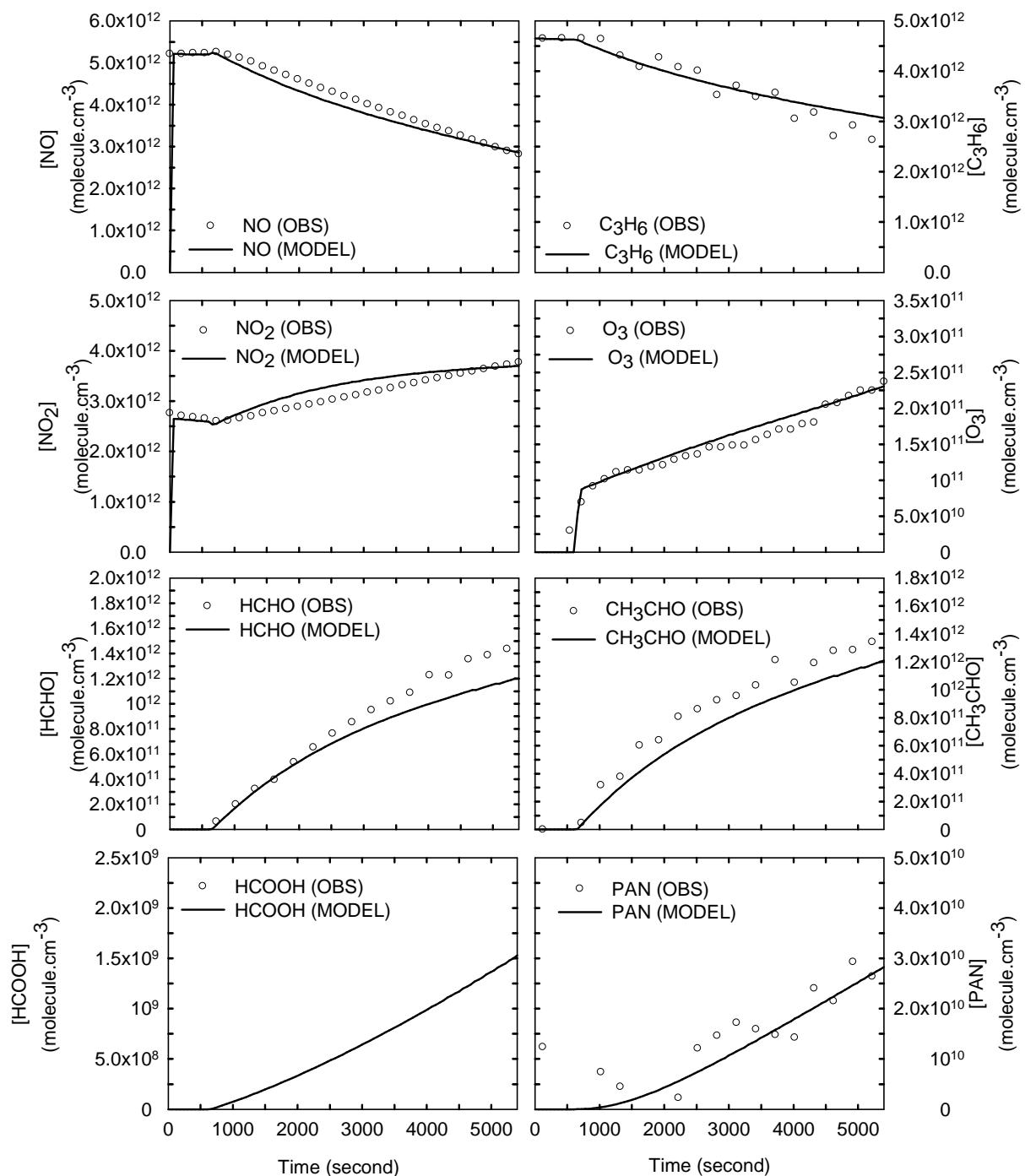
Reaction	Rate constant/unit>Status
$\text{NO}_2 \rightarrow \text{NO} + \text{O}^3\text{P}$	$J_1 / \text{s}^{-1}$ / adjusted
$\text{O}_3 \rightarrow \text{O}^1\text{D} + \text{O}_2$	$J_2 / \text{s}^{-1}$ / calculated from $J_1$ value
$\text{HONO} \rightarrow \text{OH} + \text{NO}$	$J_3 / \text{s}^{-1}$ / calculated from $J_1$ value
$\text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2$	$J_4 / \text{s}^{-1}$ / calculated from $J_1$ value
$\text{O}_3 \rightarrow \text{O}^3\text{P} + \text{O}_2$	$J_5 / \text{s}^{-1}$ / calculated from $J_1$ value
$\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}^3\text{P}$	$J_6 / \text{s}^{-1}$ / calculated from $J_1$ value
$\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$	$J_7 / \text{s}^{-1}$ / calculated from $J_1$ value
$\text{O}_2 + \text{O}^3\text{P} + \text{M} \rightarrow \text{O}_3 + \text{M}$	$6.0 \times 10^{-34} / \text{cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$
$\text{O}_3 + \text{O}^3\text{P} \rightarrow \text{O}_2 + \text{O}_2$	$8.0 \times 10^{-15} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{NO}_2 + \text{O}^3\text{P} \rightarrow \text{NO} + \text{O}_2$	$1.0 \times 10^{-11} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{NO} + \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{NO}_2$	$2.0 \times 10^{-38} / \text{cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$1.8 \times 10^{-14} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$3.5 \times 10^{-17} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	$2.6 \times 10^{-11} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{O}^1\text{D} + \text{M} \rightarrow \text{O}^3\text{P} + \text{M}$	$2.6 \times 10^{-11} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	$1.5 \times 10^{-13} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	$6.0 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{HO}_2$	$2.8 \times 10^{-13} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_3$	$7.3 \times 10^{-14} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$1.1 \times 10^{-10} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$1.6 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2$	$2.0 \times 10^{-15} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$	$8.8 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{HO}_2 + \text{NO} \rightarrow \text{HNO}_3$	$1.6 \times 10^{-14} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{H}_2\text{O} + \text{N}_2\text{O}_5 \rightarrow \text{HNO}_3 + \text{HNO}_3$	$2.5 \times 10^{-22} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$6.7 \times 10^{-15} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
$\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$	$1.8 \times 10^{-1} / \text{s}^{-1}$
$\text{NO} + \text{O}^3\text{P} \rightarrow \text{NO}_2$	$2.3 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation
$\text{NO}_2 + \text{O}^3\text{P} \rightarrow \text{NO}_3$	$2.9 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation
$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$	$1.0 \times 10^{-11} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation
$\text{OH} + \text{NO} \rightarrow \text{HONO}$	$8.3 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation
$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	$1.4 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation
$\text{HO}_2 + \text{NO}_2 \rightarrow \text{HO}_2\text{NO}_2$	$1.2 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation
$\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$	$2.1 \times 10^{-12} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation
$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$	$7.7 \times 10^{-2} / \text{s}^{-1}$ / recalculated from 2nd order equation
$\text{O}^1\text{D} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	$2.2 \times 10^{-10} / \text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ / recalculated from 3rd order equation



Comparison of simulated (solid lines) and experimental concentrations (symbols) for NO, NO<sub>2</sub>, ozone, propene, formaldehyde, acetaldehyde, formic acid and peroxyacetyl nitrate (PAN) in a propene-NOx-Air system (experiment # H0721)



Comparison of simulated (solid lines) and experimental concentrations (symbols) for NO, NO<sub>2</sub>, ozone, propene, formaldehyde, acetaldehyde, formic acid and peroxyacetyl nitrate (PAN) in a propene-NOx-Air system (experiment # N0220). Black lines are the results of modeling with an initial concentration of nitrous acid  $[HONO]_0 = 2$  ppb while continuous red lines are for  $[HONO]_0 = 3$  ppb and dashed red lines for  $[HONO]_0 = 1$  ppb.



Comparison of simulated (solid lines) and experimental concentrations (symbols) for NO, NO<sub>2</sub>, ozone, propene, formaldehyde, acetaldehyde, formic acid and peroxyacetyl nitrate (PAN) in a propene-NOx-Air system (experiment # N0306)