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Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China

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Text S1. Sensitivity tests for OBM model

The uncertainties of the measured input of NMHC, OVOCs and HONO could lead to the uncertainties of the simulated concentrations of the daytime OH radicals and also the calcuated rates of $OH+NO_2$ reaction. We carried out sensitivity tests by reducing the input concentrations by 10% to check the deviation of the average daytime (7:00-17:00) rate of $OH+NO_2$ reaction. The method of Relative Increment Reactivity (RIR) was applied here as the indicator of the sensitivity (see the following equation). R_1 means the original rate of $OH+NO_2$ reaction, while $R_{0.9}$ means the rate of $OH+NO_2$ reaction after the input concentrations were reduced to 90%.

$$RIR=\frac{(R_1-R_{0.9})/R_1}{10\%}$$

NMHCs were categorized into four groups, including C4HC, LRHC, AROM and OLF, which represent alkanes with ≥4 carbons, hydrocarbons with low reactivity (including ethane, propane and benzene), reactive aromatics (including all aromatics except for benzene), and reactive olefins (including all alkenes), respectively (Xue et al., 2014). As shown in the below figure, the simulated rate of $OH+NO_2$ reaction was most sensitive to HONO (RIR of 0.6-0.8), followed by NO_x (RIR of 0.2-0.5) and OVOCs (RIR of 0-0.2).

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Table S1. Average concentrations (ppbv) of NMHCs species during the daytime (7:00-17:00 LT) and nighttime (17:00-7:00 LT of the next day) from Jan 3 to Jan 7.

Species	Daytime	Nighttime	Species	Daytime	Nighttime
Ethane	2.257	2.310	Isoprene	0.092	0.026
Propane	7.032	6.239	Cis-2-Pentene	0.006	0.005
i-Butane	2.561	2.324	1-Hexene	0.032	0.023
n-Butane	4.879	4.588	1,3-Butadiene	0.041	0.067
i-Pentane	2.105	3.435	Benzene	0.767	0.832
n-Pentane	1.666	4.128	Toluene	5.447	6.076
2-Methylpentane	0.980	0.868	Ethylbenzene	1.313	1.812
n-Hexane	0.762	0.706	m-xylene	1.143	1.936
n-Heptane	0.307	0.273	p-xylene	1.143	1.936
n-Octane	0.085	0.068	o-xylene	0.988	1.644
Ethene	2.487	2.684	1,3,5-trimethylbenzene	0.025	0.029
Propene	0.352	0.393	1,2,4-trimethylbenzene	0.022	0.045
Ethyne	2.162	2.054	1,2,3-trimethylbenzene	0.029	0.029
trans-2-Butene	0.021	0.021	i-propbenzene	0.027	0.034
1-Butene	0.063	0.072	propbenzene	0.038	0.034
cis-2-Butene	0.024	0.027	m-ethyltoluene	0.076	0.068
1-Pentene	0.011	0.011	p-ethyltoluene	0.049	0.042
trans-2-Pentene	0.006	0.005	o-ethyltoluene	0.041	0.037

Table S2. Average values (μg m^{-3}) of $PM_{2.5}$ loadings and the composition of $PM_{2.5}$ during the time periods corresponding to Table 2 in the manuscript.

Date	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	OM	EC	$PM_{2.5}$
Jan.3 17:40-19:00	0.9	19.7	8.8	6.5	37.4	8.0	86.4
Jan 4 17:00-22:00	1.5	44.3	8.7	12.0	44.6	13.2	150.7
Jan 5 17:00-22:00	1.6	68.9	15.5	15.3	56.6	14.2	216.6
Jan 6 17:00-22:40	2.7	40.0	15.7	13.8	54.6	10.5	174.3
Jan 9 19:00-00:20	0.8	29.9	7.2	8.9	36.7	11.6	117.3

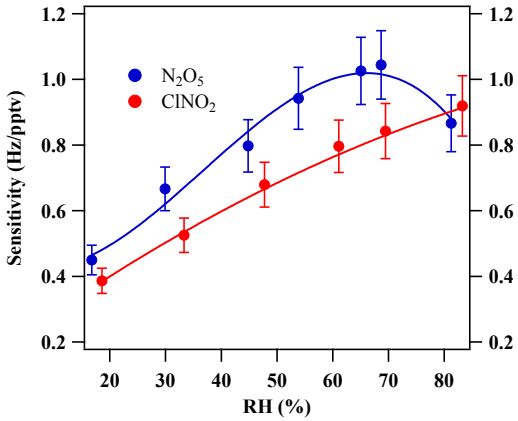

Figure S1. The sensitivity of CIMS as a function of RH for N_2O_5 at 235 m/z and $ClNO_2$ at 208 m/z at Heshan site.

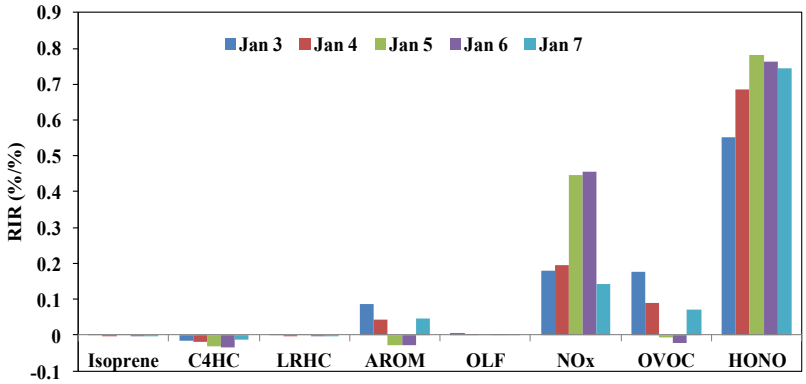

Figure S2. OBM-calculated RIRs to check the sensitivity of the average daytime (7:00-17:00) rate of $OH+NO_2$ reaction to 10% reduction of the measurement input data.

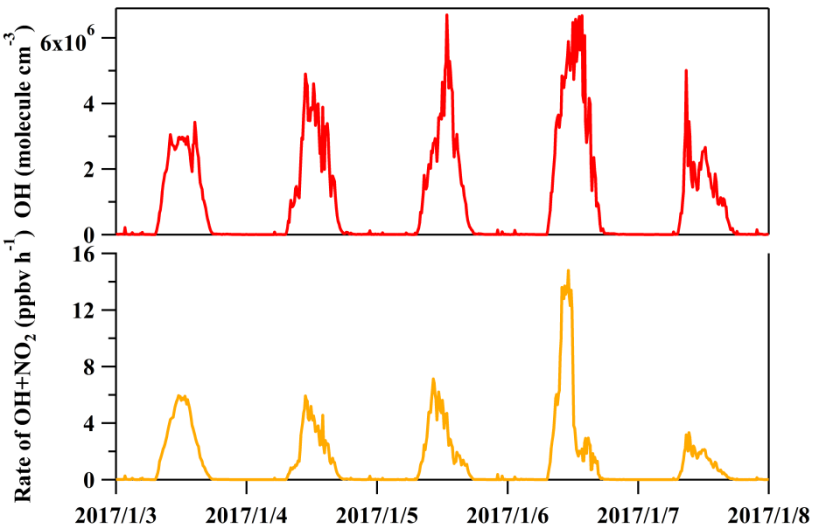

Figure S3. Variation of OH mixing ratio and the rate of OH+NO_2 from Jan 3 to Jan 7.