Supplement of OH and HO\textsubscript{2} radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018

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Table S1. α-pinene oxidation mechanism in RACM2

| Number | Reaction |
|--------|----------|
| #1     | API + OH → APIP |
| #2     | API + O₃ → 0.85 × OH + 0.1 × HO₂ + 0.2 × ETHP + 0.42 × KETP + 0.14 × CO + 0.02 × H₂O₂ + 0.65 × ALD + 0.53 × KET |
| #3     | API + NO₃ → 0.1 × OLNN + 0.9 × OLND |
| #4     | APIP + NO → 0.82 × HO₂ + 0.82 × NO₂ + 0.23 × HCHO + 0.43 × ALD + 0.44 × KET + 0.07 × ORA1 + 0.18 × ONIT |
| #5     | APIP + HO₂ → OP2 |
| #6     | APIP + MO₂ → HO₂ + 0.75 × HCHO + 0.75 × ALD + 0.75 × KET + 0.25 × MOH + 0.25 × ROH |
| #7     | APIP + ACO₃ → 0.5 × HO₂ + 0.5 × MO₂ + ALD + KET + ORA2 |
| #8     | APIP + NO₃ → HO₂ + NO₂ + ALD + KET |

API denotes α-pinene; APIP denotes peroxy radicals formed from API; ETHP denotes peroxy radicals formed from ethane; KETP denotes peroxy radicals formed from ketone; ALD denotes C3 and higher aldehydes; KET denotes ketones; OLNN denotes NO₃-alkene adduct reacting to form carbonitrates and HO₂; OLND denotes NO₃-alkene adduct reacting via decomposition; ACT denotes acetone; ORA1 denotes formic acid; ONIT denotes organic nitrate; OP2 denotes higher organic peroxides; MO₂ denotes methyl peroxy radical; MOH denotes methanol; ROH denotes C3 and higher alcohols; ACO₃ denotes acetyl peroxy radicals; ORA2 denotes acetic acid and higher acids.
Figure S1. Map of the field measurement site (red five-pointed star) in Taizhou, Jiangsu Province, which is approximately 200 km north-west and 100 km north-east of the two major megacities, Shanghai and Nanjing, in Yangtze River Delta region.

Figure S2. The mean diurnal profiles of measured and modelled PAN (a), HCHO (b), and glyoxal (c) concentrations. (a) The base model run (Base) applied a first-order loss term equivalent to a lifetime of 8 hours to all species. The other model run (w. BLH var) imposed a boundary layer height (BLH, derived from ECMWF) dependent loss rate to all species. (b) and (c) The model run (Mod) free the HCHO and glyoxal compared to the base model run (Base) in (a). The grey areas denote nighttime.
Figure S3. The mean diurnal profiles of modelled OH, HO\(_2\), RO\(_2\), and \(k_{\text{OH}}\) as well as the discrepancies (Δ) between models in different scenarios compared to base case (Scenario 1: base case; Scenario 2: w. BLH var, imposed a boundary layer height dependent loss rate to all species; Scenario 3: w. API auto, considering the isomerization of \(\alpha\)-pinene derived RO\(_2\) from \(\alpha\)-pinene and ozone reaction). Blue colored areas denote 1σ uncertainties of base case modelled radical concentrations. The grey areas denote nighttime.
Figure S4. The back trajectory cluster analysis of air masses arriving at the measurement site.

Figure S5. Results of OH chemical modulation tests performed during this campaign. In each test, the total measured OH signal without scavenger injected ($S_{N2}$) is compared with the sum of ambient OH
induced signal (SOH) and the known interference from O₃ photolysis (SO₃). The error bars denote the 1σ statistical error. A fluorescence signal of 14 cnts s⁻¹ (counts per second) corresponds to an OH concentration of 1.0×10⁷ cm⁻³.

Figure S6. The median diurnal profiles of measured and modelled OH and HO₂ concentrations. Colored areas (red) and error bars (blue) denote 1σ uncertainties of measured and base case modelled radical concentrations, respectively. The grey areas denote nighttime.
Figure S7. The mean diurnal profiles of modelled OH, HO₂, RO₂, and $k_{OH}$ as well as the discrepancies (Δ) between models in different scenarios compared to base case (Scenario 1: base case; Scenario 2: add. $k_{OH}$(MO₂), added an additional OH to MO₂ reaction with rate equivalent to 30% of total OH reactivity; Scenario 3: add. $k_{OH}$(ETEP), the same as Scenario 2, but converted OH to ETEP (peroxy radical formed from ethene); Scenario 4: add. $k_{OH}$(ACO₃), the same as Scenario 2, but converted OH to ACO₃ (acetyl peroxo radical). Blue colored areas denote 1σ uncertainties of base case modelled radical concentrations. The grey areas denote nighttime.
Figure S8. The time series of modelled ROOOH concentrations during EXPLORE-YRD campaign in 2018.

Figure S9. Dependences of the ratio of observed to modeled OH (a) and the difference between observed and modeled OH (b) on the concentration of ROOOH during daytime periods (08:00-16:00).