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Supplement of

Modeling of the chemistry in oxidation flow reactors with high initial NO

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Figure S1. Concentrations of (a, c, e) several NO$_y$ species and (b, d, f) OH, HO$_2$, O$_3$, and H$_2$O$_2$ and ratio of...
NO concentration to that of HO$_2$ as a function of reaction time in the cases shown in Fig. 1 (OFR185-iNO with 150 ppb initial NO, OFR185-iNO with 30 ppm initial NO, and OFR254-iNO with 150 ppb initial NO).
Figure S2. Same format as Fig. 1b, but at a lower initial NO level.
(a) Ratio of OH exposure in the case with input NO to that in the corresponding case (same H\_2O, UV, and OHR\_ext) without input NO for OFR185-iNO
(b) NO effective lifetime for OFR185-iNO
(c) \( \frac{r(RO_2+NO)}{r(RO_2+HO_2)} \) for OFR185-iNO
(d) NO$_3$ exposure/OH exposure for OFR185-iNO
(e) Ratio of OH exposure in the case with input NO to that in the corresponding case (same \( \text{H}_2\text{O}, \text{UV}, \text{and} \ \text{OHR}_{\text{ext}} \) without input NO for OFR254-70-iNO
(f) \( \frac{r(RO_2+NO)}{r(RO_2+HO_2)} \) for OFR254-70-iNO
(g) NO$_3$ exposure/OH exposure for OFR254-70-iNO
(h) Ratio of OH exposure in the case with input NO to that in the corresponding case (same H₂O, UV, and OHR_{ext}) without input NO for OFR254-7-iNO
\( \frac{r(RO_2+NO)}{r(RO_2+HO_2)} \) for OFR254-7-INO

(i) \( \frac{r(RO_2+NO)}{r(RO_2+HO_2)} \) for OFR254-7-INO

OHR_{ext} = 0

OHR_{ext} = 10 \text{ s}^{-1}

OHR_{ext} = 100 \text{ s}^{-1}

OHR_{ext} = 1000 \text{ s}^{-1}
(j) NO$_3$ exposure/OH exposure for OFR254-7-INO
Figure S3. Dependence of several quantities in OFR185-iNO, OFR254-70-iNO, and OFR254-7-iNO on H$_2$O and UV, for OHR$_{ext}$ of 0, 10, 100, and 1000 s$^{-1}$ (first, second, third, and fourth row of image plots in each multi-panel composite, respectively). Each multi-panel composite shows a quantity for OFR185-iNO, OFR254-70-iNO, or OFR254-7-iNO. The panels above and on the right of image plots are the line plots of the quantities shown in multi-panel composites in several typical cases. These cases are denoted in the image plots by horizontal or vertical lines of the same color and pattern as in the line plots.

In detail, the cut lines are in blue, black, dark green, and red in the plots for the cases of 0, low, high, and very high (0, 10, 100, and 1000 s$^{-1}$, respectively) external OH reactivity, respectively. Horizontal sparse-dash-dot-dot, dash-dot-dot, and dotted lines mark low, medium, and high water mixing ratios, respectively. Vertical dashed, dash-dot, and solid lines mark low, medium, and high photon fluxes, respectively. Refer to Table 2 for more details on case labels. Each multi-panel composite has a color scale corresponding to its image plots.
Figure S4. Frequency occurrence distributions of good/risky/bad high/low-NO conditions over NO effective lifetime for OFR185-iNO.
Figure S5. Frequency occurrence distributions of good high-NO conditions over physical inputs for OFR185-iNO.
Figure S6. Scatter plot of OH exposure calculated in the model with the Lambe et al. (2011) residence time distribution (OH$_{exp,RTD}$) vs. that calculated in the plug-flow model (OH$_{exp,PF}$) for OFR185-iNO, OFR254-7-iNO, and OFR254-70-iNO. 1:1, 1:3, and 3:1 lines are also shown for comparison.
Case LL

Case LM

Case LH

Case ML

Case MM

Case MH

Case HL

Case HM

Case HH

Increasing UV

Increasing H₂O
Figure S7. Same format as Fig. 4, but for the OFR185-iNO results obtained by the model with the Lambe et al. (2011) residence time distribution.
Increasing UV
Increasing H₂O

Case LL
Case LM
Case LH
Case ML
Case MM
Case MH
Case HL
Case HM
Case HH
Figure S8. Same format as Fig. 5, but for the OFR254-22-iNO results obtained by the model with the Lambe et al. (2011) residence time distribution.
Figure S9. Same as Fig. 7, but for the entire experiment (~1300 s).
(a) Gasoline vehicles, no dilution (background: Case HH)

(b) Gasoline vehicles, dilution by a factor of 100 (background: Case HH)

(c) Gasoline vehicles, dilution by a factor of 100 (background: Case HL)
(d) Diesel vehicles, no dilution (background: Case HH)

(e) Diesel vehicles, dilution by a factor of 100 (background: Case HH)

(f) Diesel vehicles, dilution by a factor of 100 (background: Case HL)
(g) Hybrid vehicles, no dilution (background: Case HH)

(h) Hybrid vehicles, dilution by a factor of 100 (background: Case HH)

(i) Hybrid vehicles, dilution by a factor of 100 (background: Case HL)

Figure S10. Similar format as Fig. 9, but without the points for the test of Karjalainen et al. (2016) and with the scatter points of emissions of individual vehicles measured by Bishop and Stedman (2013). In addition to (a–c) the scatter points of emissions of gasoline vehicles, those of (d–f) diesel and (g–i) hybrid vehicles measured by Bishop and Stedman (2013) are also shown.
S1. Rationale for selecting the criterion to quantify “high-NO” vs. “low-NO” conditions

A “high-NO” condition results in more RO2 reacted with NO than with HO2. The amount of RO2 reacted with NO, \( r(\text{RO}_2 + \text{NO}) \), is the integral of the rate of this reaction over the entire residence time, i.e.,

\[
r(\text{RO}_2 + \text{NO}) = \int_0^{t_{\text{res}}} k(\text{RO}_2 + \text{NO})[\text{RO}_2][\text{NO}] \, dt,
\]

where \( t_{\text{res}} \) is residence time, \( k(\text{RO}_2 + \text{NO}) \) is the rate constant of the reaction \( \text{RO}_2 + \text{NO} \), and \( [\text{NO}] \) and \( [\text{RO}_2] \) are RO2 and NO concentrations, respectively. The entire residence time is taken into account since there is still significant presence of VOCs after NO and primary VOCs are destroyed. The oxidation intermediates/products of primary VOCs can exist for a much longer period than NO lifetime (Nehr et al., 2014; Schwantes et al., 2017). In addition, heterogeneous OA oxidation can be important at high photochemical ages in OFR (Hu et al., 2016), leading to decomposition and revolatilization of particle-phase species. Thus continuing oxidation processes are very likely to occur during the entire the residence time.

\([\text{RO}_2]\) under a steady state approximation can be expressed as below

\[
[\text{RO}_2] = \frac{\text{OHR}_{\text{VOC}}[\text{OH}]}{k(\text{RO}_2 + \text{NO})[\text{NO}] + k(\text{RO}_2 + \text{HO}_2)[\text{HO}_2] + k(\text{RO}_2 + \text{RO}_2')[\text{RO}_2'] + \cdots},
\]

where the numerator and denominator on the right side are respectively the RO2 production rate and its total first-order RO2 loss rate constant. The production rate is simply the product of OH concentration \([\text{OH}]\) and OHR of VOC \( \text{OHR}_{\text{VOC}} \). The total loss rate constant is the sum of those of all RO2 fates (\( \text{RO}_2 + \text{NO}, \text{RO}_2 + \text{HO}_2, \text{RO}_2 + \text{RO}_2', \ldots \)).

We neglect all minor RO2 fates. \( \text{RO}_2 + \text{RO}_2' \) is also neglected since \( \text{RO}_2 + \text{RO}_2' \) cannot compete with \( \text{RO}_2 + \text{NO} \) and \( \text{RO}_2 + \text{HO}_2 \) for most \( \text{RO}_2 \) (Orlando and Tyndall, 2012), including under the typical OFR conditions, and also to focus on the relative importance of \( \text{RO}_2 + \text{NO} \) and \( \text{RO}_2 + \text{HO}_2 \). As \( k(\text{RO}_2 + \text{NO}) \) and \( k(\text{RO}_2 + \text{HO}_2) \) are very similar (Orlando and Tyndall, 2012), we assume \( k(\text{RO}_2 + \text{NO}) = k(\text{RO}_2 + \text{HO}_2) = k \). Then the \( [\text{RO}_2] \) estimation expression can be simplified as

\[
[\text{RO}_2] \approx \frac{\text{OHR}_{\text{VOC}}[\text{OH}]}{k[\text{NO}] + k[\text{HO}_2]}.
\]

Because OHR from VOC (including the reactivity of the products of the initial VOC(s)) is relatively stable for most OFR experiments (Peng et al., 2015), \( \text{OHR}_{\text{VOC}} \) is assumed to be constant here. Then \( r(\text{RO}_2 + \text{NO}) \) can be rearranged as below

\[
r(\text{RO}_2 + \text{NO}) = \text{OHR}_{\text{VOC}} \int_0^{t_{\text{res}}} \frac{[\text{OH}][\text{NO}]}{[\text{NO}] + [\text{HO}_2]} \, dt.
\]

Similarly, the amount of \( \text{RO}_2 \) reacted with \( \text{HO}_2 \), \( r(\text{RO}_2 + \text{HO}_2) \), can be obtained

\[
r(\text{RO}_2 + \text{HO}_2) = \text{OHR}_{\text{VOC}} \int_0^{t_{\text{res}}} \frac{[\text{OH}][\text{HO}_2]}{[\text{NO}] + [\text{HO}_2]} \, dt.
\]

Finally, we define “high-NO” conditions as those satisfying:
\[ \frac{r(\text{RO}_2 + \text{NO})}{r(\text{RO}_2 + \text{HO}_2)} = \int_{0}^{t_{\text{res}}} \frac{[\text{OH}][\text{NO}]}{[\text{NO}] + [\text{HO}_2]} \, dt \int_{0}^{t_{\text{res}}} \frac{[\text{OH}][\text{HO}_2]}{[\text{NO}] + [\text{HO}_2]} \, dt > 1 \]

The ratio between the two integrals on the left side of the inequality can be calculated by the model used in the present study. We thus take this inequality as the criterion for high-NO conditions in this study.

References


