Supplementary material for

Quantifying the nitrogen equilibrium and photochemistry-induced kinetic isotopic effects between NO and NO_2

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1. Chamber description, experimental setup, and control experiments

The chamber is a 10 m^3 Teflon bag equipped with several standard instruments including temperature and humidity probe, NO_x monitor and O_3 monitor. 128 wall-mounted blacklight tubes surrounded the chamber to mimic tropospheric photochemistry and the photolysis rate of NO_2 ($j(NO_2)$) when all lights are on have been previously determined to be 1.4×10^{-3} s^{-1} (Zhang et al., 2018), similar to a $j(NO_2)$ coefficient at an 81-degree solar zenith angle. The chamber was kept at room temperature and one atmospheric pressure. Before each experiment, the chamber was flushed with zero air at 40 L min^{-1} for at least 12 hours to ensure the background NO_x, O_3 and other trace gases were below detection limit.

The rate of NO_2 wall loss and the effect of NO_2+O_2 reaction were determined by conducting control experiments: 62 nmol mol^{-1} NO and 29 nmol mol^{-1} O_3 was injected into the chamber and NO, NO_2 and total NO_x concentrations were monitored. No significant decay of NO_x was and observed over a 4-hour period.

During each experiment, after the NO, NO_2 and O_3 concentrations reached steady-state, well-mixed chamber air was drawn out through a Norprene Thermoplastic tubing ~40 cm at 10 L min^{-1} and passed through a honeycomb denuder system (Chemcomb 3500, Thermo Scientific). Based on flow rate, the NO_2 reside time in the was less than 0.5 second, thus in the light-on experiments where NO and O_3 coexisted, the NO_2 produced inside the transfer tube through $NO+O_3$ reactions should be <0.03 ppb (using the upper limit of NO and O_3 concentrations in our experiments). The honeycomb denuder system consisted of two honeycomb denuder tubes connected in series. Each honeycomb denuder tube is a glass cylinder of 38 mm long, 47 mm in diameter, and consist of 212 hexagonal tubes with inner diameters of 2 mm. Before collecting sample, each denuder tube was coated with methanol solutions containing 10% KOH and 25% guaiacol, then immediately dried by passing high-purity N_2 through the denuder tube for 10 seconds. The coating on the denuder tube surface reacts with NO_2 forming NO_2^- (Williams & Grosjean, 1990). Each NO_2 collection lasted for 0.5-3 hours in order to collect enough NO_2^- for isotopic analysis (~300 nmol).

The NO_2 collection efficiency of a single honeycomb denuder tube was tested in a control experiment: air containing 66 nmol mol^{-1} of NO_2 was drawn out of the chamber through a denuder tube, and the NO_2 concentration at the exit was measured to be low than the detection limit (<1 nmol mol^{-1}), suggesting the collection efficiency was nearly 100% when $[NO_2]$ <66 nmol mol^{-1}. Furthermore, since each denuder system consisted of two denuder tubes, we tested the NO_2^- collected at the second denuder, none of them showed any measurable NO_2^-.

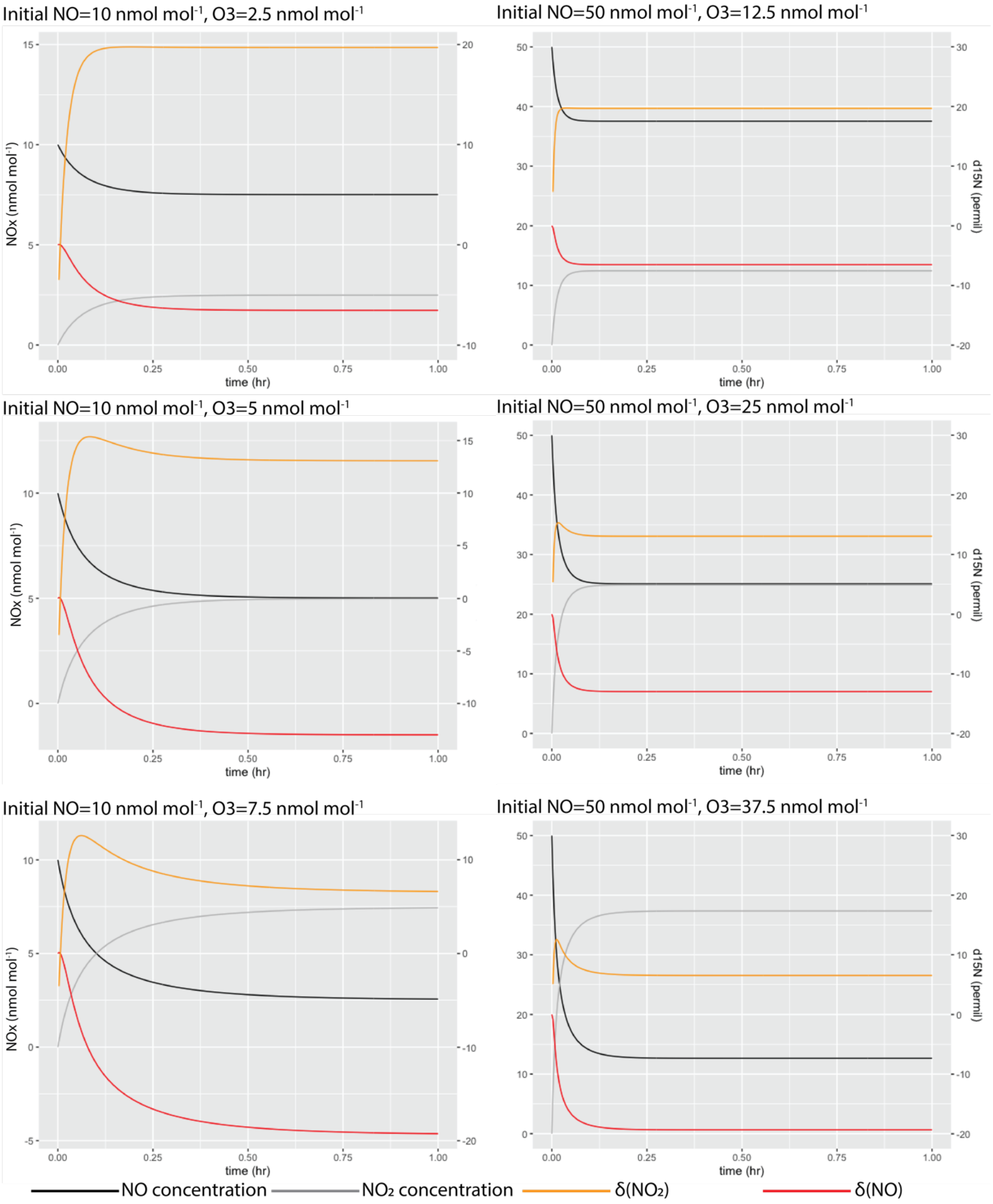
2. Box model assessing the time needed for NO-NO_2 to reach isotopic equilibrium

The time needed to reach NO-NO_2 isotopic equilibrium during light-off experiments were assessed using a 0-D box model. This box model contains only two reactions:

$^{15}NO_2 + ^{14}NO \rightarrow ^{15}NO + ^{14}NO_2$ k=8.140000 × 10^{-14} cm^3/molecules/s

$^{15}NO + ^{14}NO_2 \rightarrow ^{15}NO_2 + ^{14}NO$ k'=8.354896 × 10^{-14} cm^3/molecules/s

Where k and k' are rate constants of the reactions. The differences in rate constants were calculated by assuming an $\alpha(NO_2\text{-}NO)$ value of 1.0268. Six simulations were conducted at various initial NO (with $\delta^{15}N$=0‰) and O_3 levels that were similar to our experiment. Then the $\delta^{15}N$ values of NO and NO_2 during the simulation were calculated from the model and were shown in Fig. S1, suggesting that in our experimental condition, all systems should reach isotopic equilibrium within 1 hr.


Initial NO=10 nmol mol^{-1}, O3=2.5 nmol mol^{-1}

Initial NO=50 nmol mol^{-1}, O3=12.5 nmol mol^{-1}

Initial NO=10 nmol mol^{-1}, O3=5 nmol mol^{-1}

Initial NO=50 nmol mol^{-1}, O3=25 nmol mol^{-1}

Initial NO=10 nmol mol^{-1}, O3=7.5 nmol mol^{-1}

Initial NO=50 nmol mol^{-1}, O3=37.5 nmol mol^{-1}

Fig. S1 Simulated NO-NO$_2$ isotopic equilibrium process in the chamber at various NO and O$_3$ concentrations.

3. Deriving Equations 7 and 8

We have 6 reactions in the system:

$^{15}NO_2+^{14}NO \rightarrow ^{15}NO+^{14}NO_2$ R1, rate constant=k_1

$^{15}NO+^{14}NO_2 \rightarrow ^{15}NO_2+^{14}NO$ R2, rate constant=$k_1\times\alpha(NO_2\text{-}NO)$

$^{14}NO_2 \rightarrow ^{14}NO+O$ R3, rate constant=$j(NO_2)$

$^{15}NO_2 \rightarrow ^{15}NO+O$ R4, rate constant= $j(NO_2)\times\alpha_1$

$^{14}NO+O_3 \rightarrow ^{14}NO_2+O_2$ R5, rate constant=k_5

$^{15}NO+O_3 \rightarrow ^{15}NO_2+O_2$ R6, rate constant=$k_5\times\alpha_2$

At steady state:

$$d[^{15}NO_2]/dt=0$$

Therefore:

$$k_1\times[^{15}NO_2][^{14}NO]+j_{NO2}\times\alpha_1\times[^{15}NO_2]= k_5\times\alpha_2\times[^{15}NO]\times[O_3]+ k_1\times\alpha_{NO2\text{-}NO}\times[^{15}NO]\times[^{14}NO_2]$$

From here we refer $^{14}NO_2$ and ^{14}NO as NO_2 and NO for convenience, rearrange the above equation, we get:

$$\frac{[^{15}NO_2]}{[^{15}NO]}=\frac{k_5\times\alpha_2\times[O_3]+k_1\times\alpha_{NO2-NO}\times[NO_2]}{j_{NO2}\times\alpha_1+k_1\times[NO]}$$

Meantime, since the Leighton cycle reaction still holds for the majority isotopes (NO and NO_2), we have:

$$j_{NO2}\times[NO_2]= k_5\times[NO]\times[O_3]$$

Thus,

$$\frac{[NO_2]}{[NO]}=\frac{k_5\times[O_3]}{j_{NO2}}$$

From the text, when $j_{NO2}>0$, we defined $A=\tau_{exchange}/\tau_{photo}=j_{NO2}/(k_1\times[NO])$. using the above equation, we know:

$$\frac{j_{NO2}}{[NO]} = \frac{k_5 \times [O_3]}{[NO_2]} = A \times k_1$$

$$\frac{j_{NO2}}{k_1 \times [NO]} = \frac{k_5 \times [O_3]}{k_1 \times [NO_2]} = A$$

Next, in order to calculate $\delta(NO_2)$-$\delta(NO)$, we use the definition of delta notation:

$\delta(NO_2)-\delta(NO)=(R_{NO2}/R_{std}-1)\times1000‰-(R_{NO}/R_{std}-1)\times1000‰$;

Where $R_{NO1,2}=[^{15}NO_{1,2}]/[NO_{1,2}]$. Thus,

$(\delta(NO_2)-\delta(NO))/1000‰=R_{NO2}/R_{std}- R_{NO}/R_{std} \approx R_{NO2}/R_{NO}-1$

$$\frac{R_{NO2}}{R_{NO}} = \frac{[^{15}NO_2] \times [NO]}{[^{15}NO] \times [NO_2]} = \frac{k_5 \times \alpha_2 \times [O_3] \times [NO] + k_1 \times \alpha(NO_2 - NO) \times [NO_2] \times [NO]}{j_{NO2} \times \alpha_1 \times [NO_2] + k_1 \times [NO] \times [NO_2]}$$

Divide both side by $k_1\times[NO]\times[NO_2]$:

$$\frac{R_{NO2}}{R_{NO}} = \frac{\frac{k_5 \times \alpha_2 \times [O_3]}{k_1 \times [NO_2]} + \alpha(NO_2 - NO)}{\frac{j_{NO2} \times \alpha_1}{k_1 \times [NO]} + 1}$$

Rearrange and substitute $\frac{k_5\times[O_3]}{k_1\times[NO_2]}$ and $\frac{j_{NO2}}{k_1\times[NO]}$ with A:

$$\frac{R_{NO2}}{R_{NO}} = \frac{\alpha_2 \times A + \alpha(NO_2 - NO)}{\alpha_1 \times A + 1}$$

$$\frac{R_{NO2}}{R_{NO}} - 1 = \frac{(\alpha_2 - \alpha_1) \times A + (\alpha(NO_2 - NO) - 1)}{\alpha_1 \times A + 1}$$

Thus,

$$\delta^{15}N_{NO2}-\delta^{15}N_{NO}=\frac{(\alpha_2-\alpha_1)\times A+(\alpha(NO_2-NO)-1)}{\alpha_1\times A+1}\times1000‰$$

Since $\alpha_1 \approx 1$, $\alpha_1\times A+1 \approx 1+A$ this equation can be further simplified to Eq. 7:

$$\delta(NO_2)\text{-}\delta(NO)=\frac{(\alpha_2-\alpha_1)*A+(\alpha_{NO2-NO}-1)}{A+1}\times 1000‰$$

Then, using mass balance:

$$\delta(NO_2)\times f(NO_2)+\delta(NO)\times(1-f(NO_2))=\delta(NO_x)$$

We can derive Eq. 8:

$$\delta(NO_2)\text{-}\delta(NO_x)=\frac{(\alpha_2-\alpha_1)\times A+(\alpha_{NO2-NO}-1)}{A+1}\times(1-f(NO_2))\times 1000‰$$

References:

Williams, E. L., & Grosjean, D. (1990). Removal of atmospheric oxidants with annular denuders. *Environmental Science & Technology*, *24*(6), 811–814.

Zhang, X., Ortega, J., Huang, Y., Shertz, S., Tyndall, G. S., & Orlando, J. J. (2018). A steady-state continuous flow chamber for the study of daytime and nighttime chemistry under atmospherically relevant NO levels. *Atmospheric Measurement Techniques*, *11*(5), 2537–2551.