Supplement

S1 Impact of Product Branching Ratio for HO_2 + NO

We account for the impact of the small yield of HNO_3 from the HO_2 + NO reaction (R6b in main text) on the two HONO calibration methods. The branching ratio for these reactions is determined using literature temperature, pressure, and humidity dependences. Butkovskaya et al. (2007) present the quantity β, which is the ratio of reaction rates (k_{R7b}/k_{R7a}), rather than a traditional branching ratio ($k_{R7b}/(k_{R7a} + k_{R7b})$). First, we determine β *under dry conditions* using only the temperature and pressure dependences. This first form will be referred to as β^*.

$$\beta^*(T, P) = 0.01\left(\frac{530}{T} + 6.4\, x\, 10^{-4} \cdot P - 1.73\right) \tag{S1}$$

Where T is temperature in Kelvin and P is pressure in Torr. The 2σ uncertainties for the constants of the three numerical terms are ±10, ±1.3 and ±0.07, respectively. A humidity factor f_{H2O} is then applied to β^* to determine β (Butkovskaya et al., 2009).

$$f_{H2O} \approx (1 + 2\text{ x }10^{-17}[\mathrm{H_2O}]) \tag{S2}$$

$$\beta = f_{H2O} \cdot \beta^* \tag{S3}$$

Here, $[H_2O]$ is expressed in number concentration (molecules cm^{-3}). β is useful for accounting for the $[HNO_3]$ if the final $[NO_2]$ is observed after all HO_2 is processed by R6a and R6b:

$$\beta = \frac{\mathrm{k_{R7b}}}{\mathrm{k_{R7a}}} = \frac{[\mathrm{HNO_3}]}{[\mathrm{NO_2}]} \tag{S4}$$

$$[\mathrm{HNO_3}] = \beta \cdot [\mathrm{NO_2}] \tag{S5}$$

In the photolytic calibration involving standard O_3 actinometry, the [HOx] generated at the point of H_2O photolysis is quantified. Therefore, a branching ratio is required to account for the small portion of the HO_2 initially formed that does not form HONO because of R6b. Here, we define branching ratio as β_{BR}.

$$\beta_{Br} = \frac{\mathrm{k_{R7b}}}{\mathrm{k_{R7a}}+\mathrm{k_{R7b}}} = \frac{[\mathrm{HNO_3}]}{[\mathrm{NO_2}]+[\mathrm{HNO_3}]} \tag{S6}$$

Substituting Eq. (S5) into the $[HNO_3]$ instances in Eq. (S6) yields Eq. (S7):

$$\beta_{Br} = \frac{\beta}{1+\beta} \tag{S7}$$

This branching ratio appears in Eq. (4) in the main text.

S2 Uncertainty Propagation

Uncertainty calculations for the NO_2 proxy calibrations are mentioned in Sect. 3 of the main text. In the following sections, uncertainty equations are provided for the multipoint calibration curve (Fig. 3 of main text) and the sensitivities shown in Fig. 4 (spanning several humidity values) determined by single point calibrations.

S2.1 Multipoint Calibration Uncertainty Calculations

The multipoint calibration plot (normalized CIMS HONO signal vs quantified [HONO]) includes uncertainty in both axes. The normalized CIMS signal uncertainty (σ_{CIMS}) is quantified in Eq. (S8) by combining the relative errors of the 1 Hz CIMS $I(HONO)^-$ and I^- signals.

$$\sigma_{\mathrm{CIMS}} = \sqrt{\left(\frac{\sigma_{I(HONO)^-}}{S_{I(HONO)^-}}\right)^2 + \left(\frac{\sigma_{I^-}}{S_{I^-}}\right)^2} \tag{S8}$$

Absolute uncertainties are represented by σ, and the CIMS signals in counts per second are represented with *S*. Normalized CIMS HONO signals are scaled by a 10^6 factor for this manuscript, in which the relative error calculated by Eq. (S8) is maintained.

This quantified [HONO] uncertainty (σ_{HONO}) is calculated by Eq. (S9).

$$\sigma_{HONO} = \sqrt{\left(\frac{(\sigma_{NO_2}^2+\sigma_{NO_2}^2)^{-\frac{1}{2}}}{S_{NO_2}-bkg_{NO_2}}\right)^2 + 0.03^2 + \left(\frac{\sigma_\beta}{2+\beta}\right)^2} \tag{S9}$$

The terms added in quadrature are 1.) the background subtracted [NO_2] relative uncertainty, 2.) the CAPS NO_2 measurement accuracy (i.e. 3%), and 3.) the relative uncertainty of β as applied in Eq. (5) of the main text (i.e. including the addition of 2 as a constant). The uncertainty propagation for the NO_2 background subtraction is accomplished by combining absolute NO_2 uncertainties in quadrature (see numerator of first term) using a set value of 27 pptv for σ_{NO2} based on the 5 s average precision. The resulting absolute uncertainty in NO_2 is converted to relative uncertainty by its quotient with the background subtracted [NO_2] value (i.e. the denominator where *S* and *bkg* represent the signal and background values of [NO_2], respectively). The relative uncertainty of the third term in Eq. (S9) is very small (typically 0.14%, 2σ) due to the constant addition of 2. The value of σ_β is determined by combining the uncertainties for the variables of Eq. (S1).

S2.2 Single Point Calibration Uncertainty Calculations

The CIMS sensitivities in the Fig. 4 (of main text) single point calibration plot (showing humidity dependence) were determined by the quotient of respective background subtracted CIMS measurements with quantified [HONO] values. Therefore, the Fig. 4 uncertainties were quantified by combining in quadrature the relative errors of these two variables. The uncertainty in quantified [HONO] is calculated with Eq. (S9) - the same as discussed in Sect. S2.1. The background subtraction for the CIMS measurement is a new step (not conducted for the multipoint calibration at a single humidity) and thus requires a slightly different uncertainty calculation (Eq. (S10)) compared to Eq. (S8).

$$\sigma_{\mathrm{CIMS}} = \sqrt{\left(\frac{(\sigma_{IHONO^-}^2+\sigma_{IHONO^-_{bkg}}^2)^{-\frac{1}{2}}}{S_{IHONO^-}-bkg_{IHONO^-}}\right)^2 + \left(\frac{\sigma_{I^-}}{S_{I^-}}\right)^2} \tag{S10}$$

The first term shown in quadrature of Eq. (S10) represents the uncertainty propagation for the CIMS background subtraction process. This uncertainty propagation is handled similarly to that of the background subtraction for quantified [HONO] (see Sect. S2.1 and Eq. (S9)). First, the absolute 1 Hz uncertainties of the $I(HONO)^-$ signal and background are added in quadrature (see numerator). Then, the absolute uncertainty is converted into relative error (i.e. dividing by the background subtracted signal) to add in quadrature with the relative uncertainty of the I^- reagent signal.

References:

Butkovskaya, N., Kukui, A., and Le Bras, G.: HNO3 Forming Channel of the HO2+ NO Reaction as a Function of Pressure and Temperature in the Ranges of 72− 600 Torr and 223− 323 K, The Journal of Physical Chemistry A, 111, 9047-9053, https://doi.org/10.1021/jp074117m, 2007.

Butkovskaya, N., Rayez, M.-T., Rayez, J.-C., Kukui, A., and Le Bras, G.: Water vapor effect on the HNO3 yield in the HO2+ NO reaction: experimental and theoretical evidence, The Journal of Physical Chemistry A, 113, 11327-11342, https://doi.org/10.1021/jp811428p, 2009.