

# Referee Report:

## Evolution of NO<sub>3</sub> reactivity during the oxidation of isoprene

Anonymous Referee

### 1 Overview

Dewald et al. present measurement of NO<sub>3</sub> reactivity ( $k^{NO_3}$ ) resulting from the reaction of NO<sub>3</sub> with isoprene and stable trace gases in an atmospheric simulation chamber with different initial conditions. The agreement between  $\sum k_i[VOC]_i$  and  $k^{NO_3}$  indicates that NO<sub>3</sub> reactivity is dominated by the reaction between NO<sub>3</sub> and isoprene. Box model simulation results indicate that the discrepancy between measured  $k^{NO_3}$  and non-steady-state reactivity ( $k_{nss}^{NO_3}$ ) is caused by the uncertainty in  $k_{RO_2+NO_3}$ .

Instrument analysis is adequate. However the authors should expand the description of instrument calibration for PTR-TOF-MS (see minor comments below).

Overall, this study reports high quality data obtained from well designed experiments. The data should be of interest to the atmospheric science community. This manuscript is well within the scope of ACP. I recommend that the manuscript be published in ACP after minor revision.

### 2 Minor comments

#### (1) 2.3 VOC measurements: PTR-ToF-MS

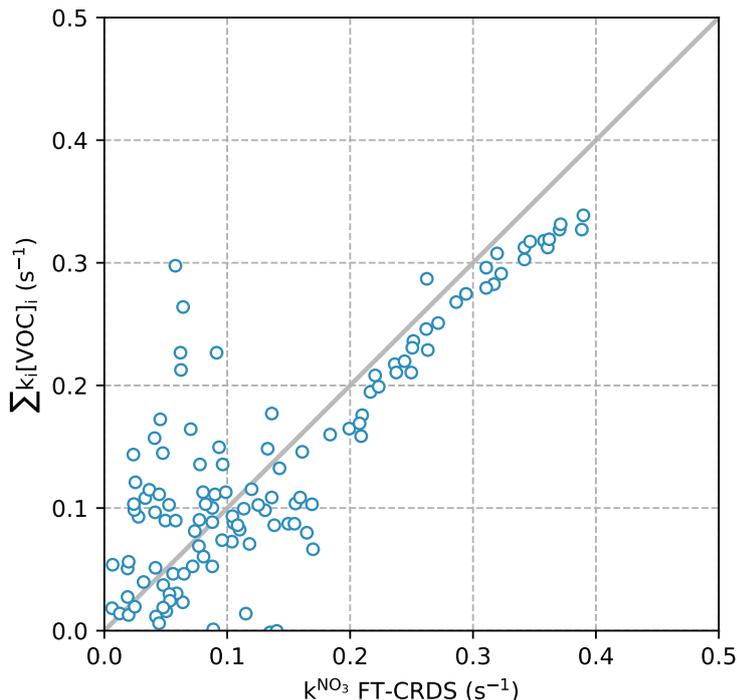
- Please describe how often were the instruments calibrated during the campaign. Please show the variability of the instrumental sensitivities during the entire campaign period;
- Please be more specific about the uncertainty used in instrument comparison. It would be useful to add a figure showing the VOCs mixing ratios measured by the two PTR-TOF-MS from the same air sample.

#### (2) 2.5 Box model: “FACSIMILE/CHEKMAT” is a dated tool. A quick search of it didn’t return much useful information. It would be great if the simulations in this study were run in an open source, modern box model, such as BOXMOX (Knote et al., 2015), FOAM (Wolfe et al., 2016), and CAABA (Sander et al., 2019). Doing so enables the reader to run the simulation on their own computer and play around with the configurations, such as the reaction rate constant $k_{RO_2+NO_3}$ , the wall loss rates of NO<sub>3</sub> etc.

#### (3) Page 8, Line 227: “no propene data was available”: is this due to the unavailability of propene in the standard gas? If so, the expected sensitivity of propene can be calculated using the method described in Holzinger et al. (2019). The

uncertainty of propene mixing ratios introduced from using expected sensitivity should be smaller than using model estimation. Please justify why the propene mixing ratios were assessed with the model instead of calculated using its sensitivity.

- (4) Page 8, Line 242: Please provide output from the unweighted linear regression (e.g., correlation coefficient, p-value), and incorporate the output into your discussion on the agreement between  $\sum k_i[VOC]_i$  and  $k^{NO_3}$  measurements.
- (5) Page 13, Line 388–395:
  - Please merge the model output (with  $k_{wall} = 0 \text{ s}^{-1}$ ) in Figure S3 to Figure 9, this could help the reader better visualize the effect of introducing the  $NO_3$  and  $N_2O_5$  wall loss;
  - Please discuss more about the effect of omitting the  $NO_3$  and  $N_2O_5$  wall loss and its cause of large discrepancies between the measurement and model simulation in  $NO_3$ ,  $N_2O_5$ , and isoprene mixing ratios;
  - Please discuss how is the first-order wall loss rate for  $O_3$ ,  $H_2O_2$ ,  $HO$ ,  $HONO$  and  $HNO_3$  derived in Table S1.
- (6) Page 13, Line 391: “and isoprene (following its addition at 10:50)”: from Figure 9 and Figure S2,  $NO_2$  appeared to be injected at 10:50, isoprene appeared to be injected at 11:00, please clarify.
- (7) Page 22, Figure 2(b): To better aid visual inspection of the dataset, please set the aspect ratio of x:y to 1:1, add grid to x-axis and y-axis, add border to the legend (not shown in the demo below). See Figure 2(b).



**Figure 2(b).** Correlation between  $\sum k_i[VOC]_i$  and  $k^{NO_3}$  measurements. For demo purpose only, dataset are not categorised according to sampling days, no legend is shown, no linear regression result is shown.

## References

- Holzinger, R., Acton, W. J. F., Bloss, W. J., Breitenlechner, M., Crilley, L. R., Dusanter, S., Gonin, M., Gros, V., Keutsch, F. N., Kiendler-Scharr, A., Kramer, L. J., Krechmer, J. E., Languille, B., Locoge, N., Lopez-Hilfiker, F., Materić, D., Moreno, S., Nemitz, E., Quéléver, L. L. J., Sarda Esteve, R., Sauvage, S., Schallhart, S., Sommariva, R., Tillmann, R., Wedel, S., Worton, D. R., Xu, K., and Zaytsev, A.: Validity and limitations of simple reaction kinetics to calculate concentrations of organic compounds from ion counts in PTR-MS, *Atmospheric Measurement Techniques*, 12, 6193–6208, <https://doi.org/10.5194/amt-12-6193-2019>, <https://www.atmos-meas-tech.net/12/6193/2019/>, 2019.
- Knote, C., Tuccella, P., Curci, G., Emmons, L., Orlando, J. J., Madronich, S., Baró, R., Jiménez-Guerrero, P., Luecken, D., Hogrefe, C., Forkel, R., Werhahn, J., Hirtl, M., Pérez, J. L., Roberto, Giordano, L., Brunner, D., Yahya, K., and Zhang, Y.: Influence of the choice of gas-phase mechanism on predictions of key gaseous pollutants during the AQMEII phase-2 intercomparison, *Atmospheric Environment*, 115, 553–568, <https://doi.org/https://doi.org/10.1016/j.atmosenv.2014.11.066>, <http://www.sciencedirect.com/science/article/pii/S1352231014009388>, 2015.
- Sander, R., Baumgaertner, A., Cabrera-Perez, D., Frank, F., Gromov, S., Grooß, J.-U., Harder, H., Huijnen, V., Jöckel, P., Karydis, V. A., Niemeyer, K. E., Pozzer, A., Riede, H., Schultz, M. G., Taraborrelli, D., and Tauer, S.: The community atmospheric chem-

istry box model CAABA/MECCA-4.0, Geoscientific Model Development, 12, 1365–1385, <https://doi.org/10.5194/gmd-12-1365-2019>, <https://www.geosci-model-dev.net/12/1365/2019/>, 2019.

Wolfe, G. M., Marvin, M. R., Roberts, S. J., Travis, K. R., and Liao, J.: The Framework for 0-D Atmospheric Modeling (F0AM) v3.1, Geoscientific Model Development, 9, 3309–3319, <https://doi.org/10.5194/gmd-9-3309-2016>, <https://www.geosci-model-dev.net/9/3309/2016/>, 2016.