Model Calculation of MVK, MACR and HCHO Yields

In Section 3 of the main text, we utilize model-derived first-generation yields of MVK and MACR to infer initial isoprene mixing ratios. Yields are calculated using the University of Washington Chemical Box Model (UWCMv2.2, described further in Sect. 5) driven by the Master Chemical Mechanism (MCMv3.3.1, (Jenkin et al., 2015)). The model is set up to simulate a series of pseudo-chamber experiments as follows. Meteorology is set to typical daytime surface conditions for the SENEX location and period (P = 1000 mbar, T = 298 K, RH = 75%, solar zenith angle = 10°). Mixing ratios of CO and O₃ are respectively held constant at 120 ppbv and 50 ppbv. Mixing ratios of isoprene, OH, HO₂ and NO₂ are respectively initialized at 5 ppbv, 0.04 pptv (2.7 x 10⁶ cm⁻³), 20 pptv and 4*[NO] and allowed to evolve in time. An additional constant HO₂ source, equivalent to photolysis of 5 ppbv HCHO, is also introduced to compensate for missing HO₂ sources that would be present under real atmospheric conditions. This modification, along with allowing OH and HO₂ to vary with NOₓ, provides better representation of the NOₓ-dependent fate of RO₂. NO mixing ratios are held fixed at values ranging from 1 pptv to 10 ppbv. For each NO value, the model is integrated forward for one hour. First-generation yields for MVK, MACR and HCHO are calculated as the slope of the relationship between isoprene lost and product gained, i.e. \( y = \frac{\Delta[\text{product}]}{\Delta[\text{isoprene}]} \). The fitting window is restricted to minutes 5 – 10 of the simulation to minimize effects of model spin-up and multi-generation chemistry. Resulting yield curves are shown in Fig. S3A. Model-derived yields of MVK and MACR are consistent with recent lab-derived yields at both high (Liu et al., 2013) and low (Fuchs et al., 2013) NOₓ. Within the range of NO mixing ratios observed during SENEX, simulated OH, HO₂ and RO₂ values (Fig. S3B) are comparable to those calculated in the full 0-D steady-state simulation (Sect. 5) and we have good confidence in the accuracy of calculated yields. Outside of this range (< 20 pptv NO), calculated yields are less certain due to a lack of constraints on model HO₂ and RO₂ concentrations.

References

Fuchs, H., Hofzumahaus, A., Rohrer, F., Bohn, B., Brauers, T., Dorn, H., Haseler, R., Holland, F., Kaminski, M., Li, X., Lu, K., Nehr, S., Tillmann, R., Wegener, R., and Wahner, A.:


Figure S1. (A) Comparison of PTR-MS and iWAS observations of the sum of MVK+MACR. PTR-MS observations are averaged over the iWAS sampling start and stop times. Dashed line shows the 1:1 correlation axis, and solid blue line and text is a major axis least-squares fit that minimizes residuals in both dimensions. Quoted fitting uncertainties are 1σ. (B) same as (A) but with a correction to iWAS assuming a 50% conversion efficiency of ISOPOOH (see Fig. S2).
**Figure S2.** Correspondence between ISOPOOH mixing ratios (nominally C$_5$H$_{10}$O$_3$) and the ratio (A) or difference (B) of iWAS and PTR-MS measurements of MVK+MACR. Solid blue lines and text represent simple least-squares fits with their 1σ uncertainty. Dotted lines are guides for the eye.
Figure S3. (A) NO dependence of the first-generation yields of HCHO, MVK and MACR from isoprene oxidation. Yields are derived from box model calculations using MCMv3.3.1 chemistry as described in the SI text. Thin green vertical lines denote, from left to right, the 1st, 5th, 50th, 95th and 99th percentiles of daytime boundary layer NO observed during SENEX. (B) Model-calculated concentrations of OH, HO$_2$ and total RO$_2$ for the yield simulations. Concentrations are averaged over the 300 – 600 s yield fitting window for each NO value. The minimum OH concentration is $\sim 1.4 \times 10^6$ cm$^{-3}$. 
Figure S4. (A) Photochemical exposures (product of OH concentration and reaction time) derived from PTR-MS observations of the sum and MVK and MACR as described in Sect. 3 of the main text. PTR-MS measurements are partitioned into MVK and MACR using the MVK/MACR ratio derived from a 0-D box model simulation. The dashed line denotes a 1:1 relationship. (B) Comparison of observed and initial isoprene mixing ratios. Dashed lines denote slopes for different ratios of initial to observed isoprene.
Figure S5. Comparison of observed and modeled HCHO mixing ratios for (A) the AM3 global chemical transport model and (B) the UWCM 0-D box model. Observations and model results are averaged/simulated at 1-minute resolution and filtered to only include daytime, boundary layer, non-biomass burning regions. Dashed lines represent the 1:1 correlation, and solid blue lines represent major axis least-squares fits. Corresponding slopes, intercepts and coefficients of determination ($r^2$) are also shown with their 1σ fitting uncertainty.
Figure S6. Fractional contributions of NO, HO$_2$, RO$_2$ and isomerization to total ISOPO2 loss as a function of NO. Loss fractions for MCMv3.3.1 (A) are calculated by extracting instantaneous rates for all 7 ISOPO$_2$ isomers from the yield simulations described in Section S1 and averaging these over the same timeframe used to calculate yields (300 – 600 s). Loss fractions for AM3 (B) are calculated using the NO, HO$_2$ and RO$_2$ mixing ratios from the same simulation (Fig. S3B) and rate constants provided on the GEOS-chem wiki (http://wiki.seas.harvard.edu/geos-chem/index.php/New_isoprene_scheme, last accessed 20 January 2016).
Figure S7. Comparison of absolute ISOPO$_2$ reactivities for the AM3 (black solid line) and MCMv3.3.1 (red dashed line) chemical mechanisms against reaction with NO (A), HO$_2$ (B), RO$_2$ (C) and isomerization (D). Reactivities are calculated using the methods described in the Fig. S6 caption. Also shown is the total ISOPO$_2$ lifetime (E).