Supplementary Information

For the manuscript entitled “Evaluation of 1,3,5 trimethylbenzene degradation in the detailed tropospheric chemistry mechanism, MCMv3.1, using environmental chamber data” presented by Metzger et al.

A. Description of the HCHO measurements using the Hantzsch method

Briefly, HCHO is collected in a glass coil scrubber. The scrubbing solution is mixed with the Hantzsch solution (mixture of acetic acid, acetyl acetone and ammonium acetate). A fluorescent derivative is formed from a reaction of formaldehyde with ammonium acetate and acetyl acetone in a heated reaction coil. The produced diacetyldihydrolutidine (DDL) is then detected by fluorimetry. The excitation and emission wavelengths are 400 and 510 nm.

B. Cross calibrations of the PTR-MS and IC-MS technique using a nitrous acid (HONO) source:

HONO was produced by reaction of a sodium nitrite solution with sulphuric acid in a flow system where a carrier gas was passed through the mixture continuously purging nitrous acid vapour out (Taira and Kanada, 1990).

HONO was continuously measured with the PTR-MS and the HONO signal was derived from the difference between signals with and without the scrubber. HONO mixing ratios are then calculated from the following equation, taking into account the mass dependent transmission of the instrument (Steinbacher et al., 2004):

$$[VOC] = \frac{[VOCH^+]trans(H_3O^+)}{[H_3O^+]trans(VOCH^+)kt} \tag{3}$$

where t is the residence time of the primary ions in the drift tube, k is the proton-transfer reaction rate constant and trans (. . .) is the mass dependent transmission for the respective ions. $[VOCH^+]$ and $[H_3O^+]$ are taken from the ion signals of the protonated VOC. HONO concentrations were calculated using a k-value of 2.7×10^{-9} cm^3s^{-1} (Wisthaler et al., 2005). As shown in Fig A1 calculated PTR-MS concentrations are in excellent agreement with the IC-MS data for this calibration exercise.

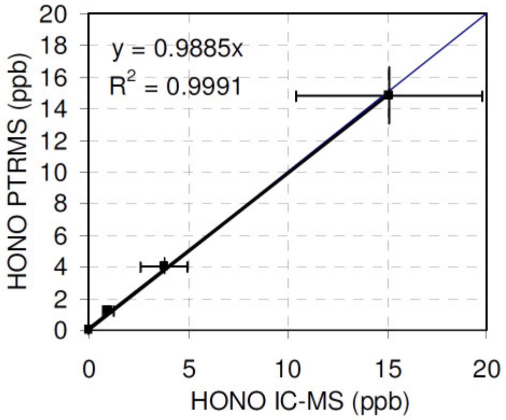

Figure B1: Cross calibrations of the PTR-MS and IC-MS technique using a pure HONO source. Calculated PTR-MS concentrations are in excellent agreement with the IC-MS. Data points with corresponding accuracy of the IC-MS (31%) and 3-sigma precision of the PTR-MS signal. PTR-MS HONO concentrations were derived by calculation using simple pseudo first-order ion-molecule reaction kinetics for a k-value of 2.7×10^{-9} cm^3s^{-1}.

Appendix C: Model - measurement comparison for a CO-NO$_x$ air experiment

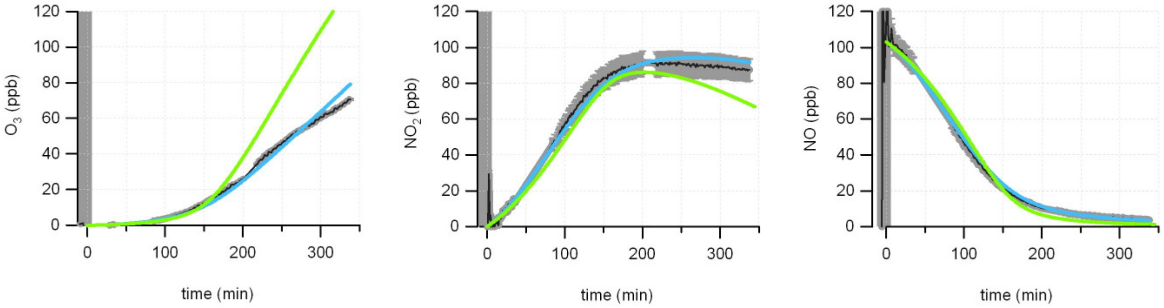

Figure C1: Model - measurement comparison for a CO-NO$_x$ air experiment. Shown are the time traces for NO, NO$_2$ and ozone. Simulations with the base case (blue line) and the tuned (green line) mechanism are shown.

Appendix D: Model error in peak ozone concentration

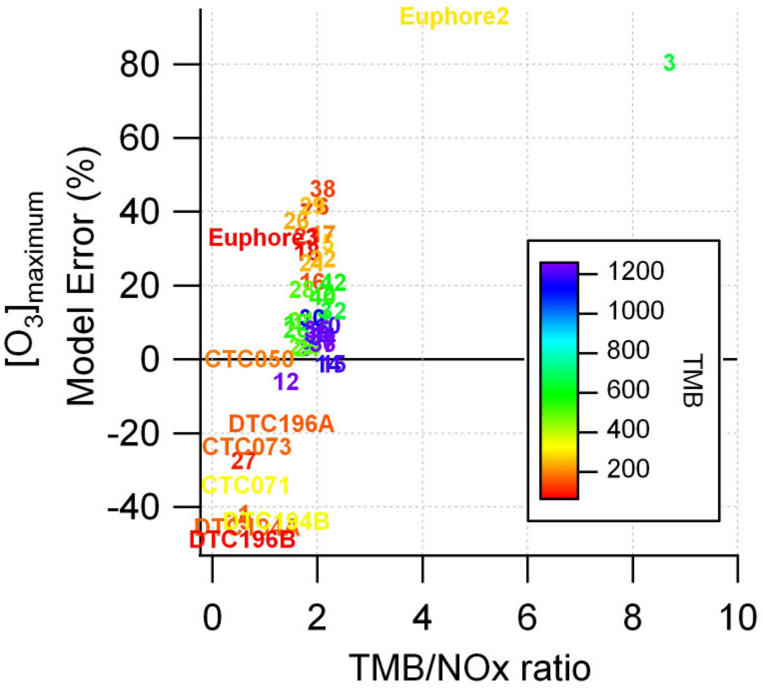

Figure D1: Model error in peak ozone concentration independent of the timing, plotted vs. the initial TMB/NO$_x$ ratio.

References

Steinbacher, M., Dommen, J., Ammann, C., Spirig, C., Neftel, A., and Prevot, A. S. H.: Performance characteristics of a proton-transfer-reaction mass spectrometer (PTR-MS) derived from laboratory and field measurements, International Journal of Mass Spectrometry, 239, 117-128, 2004.

Taira, M., and Kanda, Y.: Continuous Generation System for Low-Concentration Gaseous Nitrous-Acid, Anal. Chem., 62, 630-633, 1990.

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