Supplementary Information for: Analysis of High Mass Resolution PTR-TOF Mass Spectra from 1,3,5-Trimethylbenzene (TMB) Environmental Chamber Experiments

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1 Quantification

PTR-TOF calibrations were performed at regular intervals using multi-component gas cylinders (Apel Riemer Environmental Inc., Denver, USA). During calibration, the sample air humidity was kept at similar levels as measured in the environmental chamber. Calibrated sensitivities for several chemical groups, including alcohols, aromatic compounds, aldehydes and ketones, were used as a basis for VOC quantification (Table S1). Proton transfer reaction rate coefficients for compounds not accessible to direct calibration were calculated from the dipole moment μ_D and polarizability α of the molecule using the parameterized reaction rate theory (k_{SC}) by Su and Chesnavich (1982). Quantum chemical Gaussian 09 DFT calculations were performed to obtain the dipole moment μ_D and the polarizability α of the primary reaction products expected from the MCMv3.1 (Table S2). Calculated rates of the expected products were linked to experimental calibration results. The products were grouped into acetone-like compounds ($k_{SC} > 2.9\ 10^{-9}$ cm^3 s^{-1}), e.g. 3,5-dimethylbenzaldehyde and 3,5-dimethyl-3(2H)-2-furanone, and xylene-like compounds ($1.9 < k_{SC} < 2.4\ 10^{-9}$ cm^3 s^{-1}), e.g. 2,4,6-trimethylphenol and 2-methyl-4-oxo-2-pentenal. These compounds were quantified using measured acetone and xylene sensitivities, respectively. In case of mass spectrometrically not separable compounds, i.e. the $C_6H_9O_2^+$ isomers 3,5-dimethylfuran-2(5H)-one ($k_{SC} = 3.05\ 10^{-9}$ cm^3 s^{-1}) and (E)-2-methyl-4-oxopent-2-enal ($k_{SC} = 1.96\ 10^{-9}$ cm^3 s^{-1}), the total measured signal was quantified as an acetone-like compound. It is likely that these concentrations are underestimated. All unidentified ions were quantified as acetone-like compounds. The major primary reaction product, methylglyoxal, has a very low dipole moment ($\mu_D = 0.992$ D) and does not react with protonated water clusters $(H_2O)_nH^+$ (n > 1). Ion chemistry kinetics is thus similar to benzene and benzene sensitivities were used as a proxy for both E/N = 135 and 90 Td (1 Td = 10^{-17} V cm²) methylglyoxal quantification. Expected uncertainties are ± 15% for TMB, ± 20 % for methylglyoxal and ± 30 % for all other primary reaction products.

2 Fragmentation of ions

PTR is generally referred to as a soft ionization method. The elemental composition of each VOC is conserved in the respective protonated ion ($VOC.H^+$). Nevertheless, for many compounds fragmentation or hydration of the $VOC.H^+$ ion can occur which limits the quantification and identification capability of PTR-MS. A well-known dissociative process is H_2O loss upon protonation (e.g. from alcohols and aldehydes; de Gouw et al., 2003). This reaction can be very effective and may result in very low $VOC.H^+$ abundances. Loss or addition of H_2O will not affect the number of carbon atoms of a compound, but it will affect the measured atomic O:C ratio. To better identify hydrated or dehydrated ions, we performed measurements at two different E/N settings (90 Td and 135 Td). Hansel and Wisthaler (2000), D'Anna et al. (2004) and Aoki et al. (2007) found that nitrooxy-group ($-ONO_2$) containing compounds are prone to the loss of HNO_2 and/or HNO_3 or form NO_2^+ ions losing all carbon in the neutral fragment. A small fraction of the $VOC.H^+$ ions does not dissociate, which can be used to qualitatively follow the temporal evolution of PANs and nitrates. No ionic fragmentation pathways have been reported for MCM expected products grouped as "peroxide-bicyclic" and "epoxy-oxy" compounds. Aprea et al. (2006) reported strong fragmentation of esters in the PTR-MS drift tube which is characterized by the opening of the C-O-C oxygen bridge. A similar loss of carbon and oxygen is expected for "peroxide-bicyclic" and "epoxy-oxy" compounds.

Although operation at 400 V and 600 V drift tube voltage helped to identify potential ion fragments and water clusters, it is likely that the measured total product carbon signal and O:C ratios are underestimated, especially for highly functionalized degradation products.

References

Aoki, N., Inomata, S., and Tanimoto, H.: Detection of C-1-C-5 alkyl nitrates by proton transfer reaction time-of-flight mass spectrometry, Int. J. Mass Spectrom., 263, 12-21, 10.1016/j.ijms.2006.11.018, 2007.

Aprea, E., Biasioli, F., Sani, G., Cantini, C., Mark, T. D., and Gasperi, F.: Proton transfer reaction-mass spectrometry (PTR-MS) headspace analysis for rapid detection of oxidative alteration of olive oil, J. Agric. Food Chem., 54, 7635-7640, 10.1021/jf060970r, 2006.

D'Anna, B., Wisthaler, A., Andreasen, O., Hansel, A., Hjorth, J., Jensen, N. R., Nielsen, C. J., Stenstrom, Y., and Viidanoja, J.: Atmospheric chemistry of C-3-C-6 cycloalkanecarbaldehydes, J. Phys. Chem. A, 109, 5104-5118, 10.1021/jp044495g, 2005.

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, Int. J. Mass Spectrom., 223, 365-382, 2003.

Hansel, A., and Wisthaler, A.: A method for real-time detection of PAN, PPN and MPAN in ambient air, Geophys. Res. Lett., 27, 895-898, 2000.

Su, T., and Chesnavich, W. J.: Parametrization of the ion-polar molecule collision rate-constant by trajectory calculations, J. Chem. Phys., 76, 5183-5185, 1982.

Tables

Table S1. Sensitivities in normalized (10^6 primary ions) counts per second per ppbv for 600 V and 400 V drift tube voltages.

m/z	**compound**	**600 V**	**400 V**
		[ncps/ppbv]	
33.03	methanol	17.4	7.3
42.03	acetonitrile	36.0	29.1
47.05	ethanol	3.2	14.1
51.04	methanol cluster	1.0	24.9
59.05	acetone	40.5	28.1
60.04	acetonitrile cluster	1.6	21.9
65.06	ethanol cluster	0.1	23.6
69.07	isoprene	22.8	23.5
73.07	butanol	44.1	0.8
77.06	acetone cluster	0.1	11.3
79.05	benzene	23.5	4.5
81.07	α-pinene fragment	13.2	3.2
83.09	hexanol fragment	26.3	4.6
93.07	toluene	29.6	15.2
101.1	hexanol	3.6	28.2
107.09	xylene	33.0	25.3
119.11	hexanol cluster	0.1	16.1
137.13	α-pinene	17.9	24.6

Table S2. Dipole moment μ_D, polarizability α and reaction rate coefficient k_{SC} for selected MCM expected primary products.

compound	**m/z**	**μ_D [D]**	**α [Å³]**	**k_{SC} [10^{-9}cm^{2}s^{-1}]**
3,5-dimethylbenzaldehyde	134	4.26	13.01	3.08
1,3-dimethylbenzene	106	0.38	11.12	1.98
2,4,6-trimethylphenol	136	1.47	13.28	2.28
methyl maleic anhydride	112	5.49	7.69	3.37
3,5-dimethyl-3(2H)-2-furanone	112	4.60	8.89	3.05
2-methyl-4-oxo-2-pentenal	112	1.25	9.57	1.97
3,5-dimethyl-5(2H)-2-furanone	112	5.50	9.03	3.45
3-methyl-5-methylidene-5(2H)-2-furanone	110	4.97	9.73	3.27
methylglyoxal	72	0.99	4.78	1.47