

SOA originating from the oxidation of 1,3,5-trimethylbenzene

Maria Rodigast, Anke Mutzel,
Yoshiteru Iinuma, Olaf Böge, Hartmut Herrmann

Leibniz-Institute for Tropospheric Research, Leipzig, Germany



Introduction

Volatile organic compounds (VOCs) are emitted from biogenic and anthropogenic sources in large quantities (1300 Tg carbon year⁻¹; Hallquist et al., 2009). The oxidation of VOCs in the atmosphere leads to the formation of semivolatile organic compounds which can partition into the particle phase contributing to the formation of secondary organic aerosol (SOA). Literature studies have shown a discrepancy of the global SOA burden between model and field studies (Goldstein and Galbally, 2007). This discrepancy might be caused by so far unknown SOA sources. Thus, it is most likely that the oxidation of VOCs and their oxidation products within the aqueous phase (aqSOA) has to be considered as an additional source of SOA (Ervens et al., 2011, Herrmann et al., 1999). For this reason the oxidation of 1,3,5-trimethylbenzene (1,3,5-TMB) and the corresponding oxidation products in the gas-, particle- and aqueous phase was investigated to discriminate between SOA formed by gas phase oxidation and aqSOA.

Measurements

Aerosol chamber experiments

The experiments were conducted in the 19 m³ aerosol chamber LEAK (LEipzig Aerosol Kammer; S/V = 2 m⁻¹; Figure 1). OH radicals were formed during the photolysis of nitrous acid (HONO) ($\lambda = 336$ nm). The oxidation was conducted under various relative humidities (RH = 0%, 30%, 50%) and in the presence of NH₄H₂SO₄ seed particles (78 mmol L⁻¹).

The mixing ratios of the precursor compound and the gas phase products were measured with a proton-transfer-reaction mass spectrometer (PTR-MS) and the particle size distributions of the seed particles were measured with a SMPS (Scanning Mobility Particle Sizer). After the experiments 1.8 m³ of the chamber volume were sampled with a denuder/filter device.

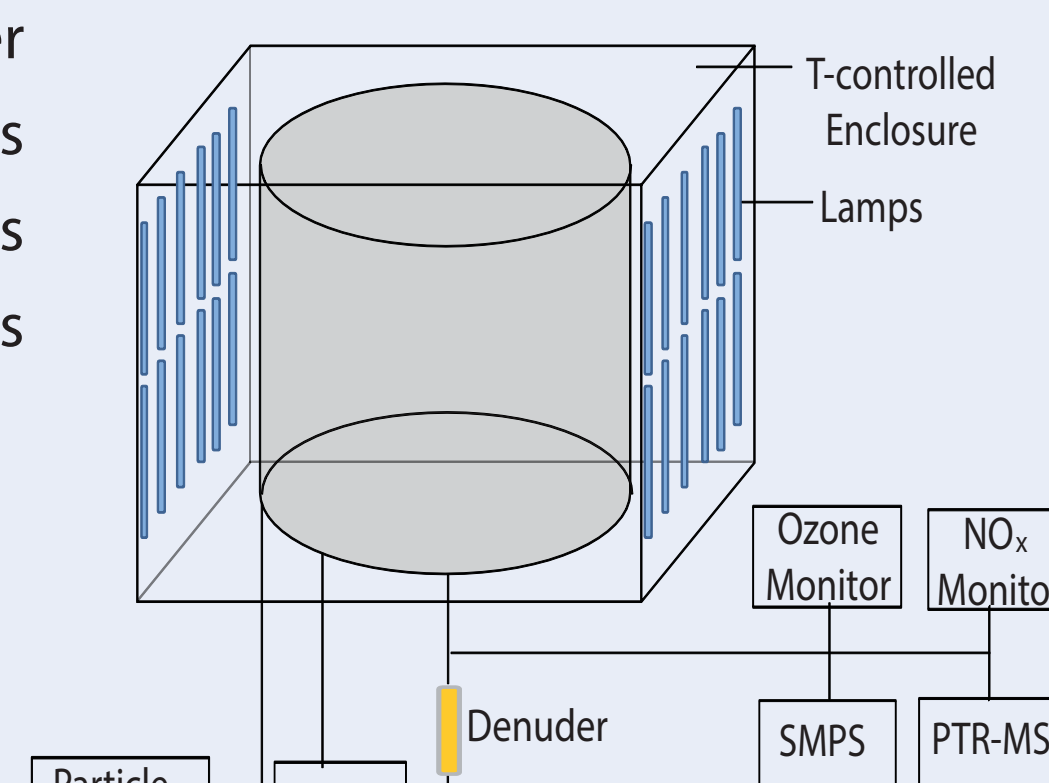


Figure 1: Aerosol chamber LEAK.

Table 1: Conditions of the experiments in LEAK.

Precursor compound	T [K]	RH [%]	Seed particle	Δ H [ppb]	γ_{SOA} [%]
1,3,5-TMB	294	0	78 mmol L ⁻¹ NH ₄ H ₂ SO ₄	29	2.1
1,3,5-TMB	294	30	78 mmol L ⁻¹ NH ₄ H ₂ SO ₄	27	2.3
1,3,5-TMB	294	50	78 mmol L ⁻¹ NH ₄ H ₂ SO ₄	27	0.1

Bulk reactor experiments

Experiments in the aqueous phase were conducted in a 300 mL bulk reactor (Figure 2). Hydrogen peroxide was used to produce OH radicals by photolysis at $\lambda = 254$ nm using a xenon/mercury lamp. During the experiments 3 mL samples were taken at t = 0, t = 1 h, t = 2 h, t = 3 h, t = 4 h, t = 5 h, t = 6 h, t = 7 h, t = 8 h over the course of the experiment (3mL).

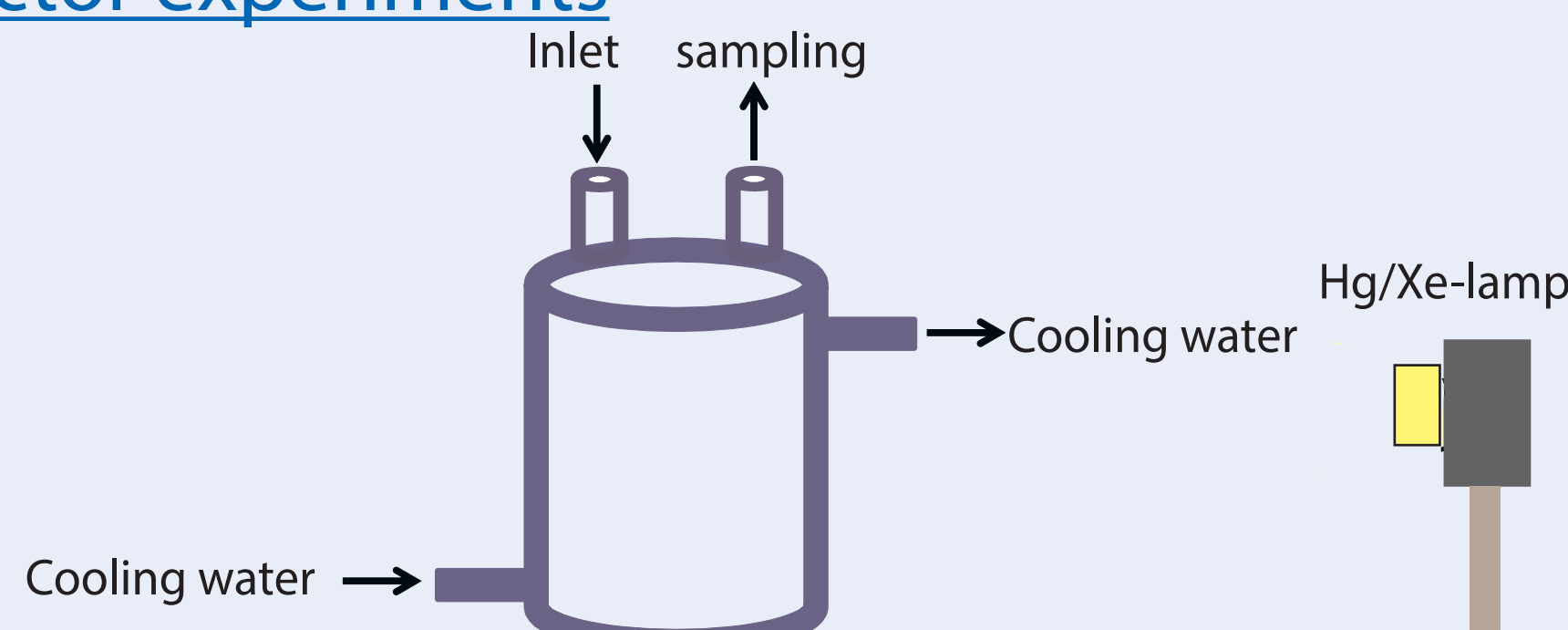


Figure 2: Experimental setup for aqueous phase experiments.

Sample preparation

Aerosol chamber experiments

The gas- and particle phase products were sampled on a teflon coated borosilicate filter combined with a XAD-4/DNPH (2,4-dinitrophenylhydrazine) coated denuder. The denuder samples were extracted three times with 50 mL acetonitrile. The extract was dried under a nitrogen stream at 10°C and purified with solid phase micro extraction (SPE). After SPE the samples were reconstituted in 500 μ L acetonitrile/water (50/50, v/v).

The filters were cut in small pieces and one half was extracted with 2.5 mL acetonitrile. Afterwards 100 μ L DNPH (0.02 mol L⁻¹ DNPH solution; 0.87 mol L⁻¹ phosphoric acid) and 50 μ L internal standard (100 μ Mol L⁻¹ of 2-(trifluoromethyl)benzaldehyde-DNPH in acetonitrile) were added. The extracted samples were dried under a nitrogen stream at 10°C and purified with SPE. After SPE the samples were dried again and reconstituted in 500 μ L acetonitrile/water (50/50, v/v).

The denuder and filter samples were analysed with high-performance-liquid chromatography electrospray ionisation time of flight mass spectrometry (HPLC/(-)ESI-TOFMS) and identified with authentic standard compounds (Figure 3).

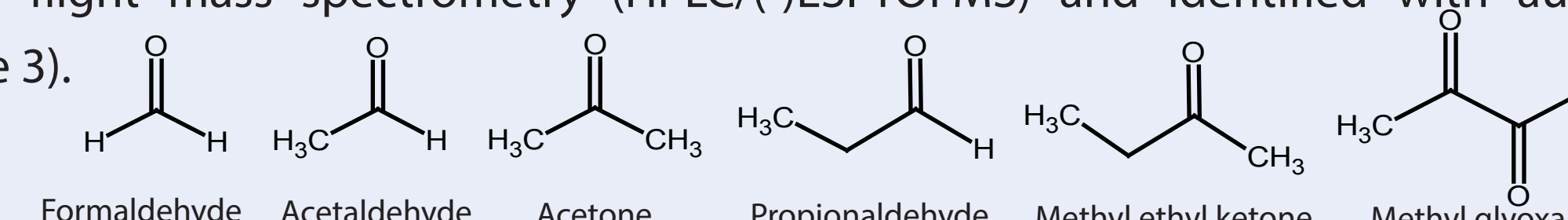


Figure 3: Authentic standard compounds to identify and quantify carbonyl compounds found after DNPH derivatisation of the denuder and filter samples.

Bulk reactor experiments

The aqueous phase samples were derivatised with PFBHA (O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine). 5 mg of PFBHA was solved in 1 mL water and 300 μ L of the derivatisation reagent (0.02 mol L⁻¹) and 150 μ L of the internal standard (0.03 mol L⁻¹ of 2-(trifluoromethyl)benzaldehyde) were added to the samples. After 24 hours 60 μ L hydrochloric acid (36%) were added and the samples were extracted with 250 μ L dichloromethane. The organic phase was analysed with gas chromatography electron impact quadrupole mass spectrometry (GC/MS).

Results and Discussion

Product study

Among the detected products few were found which could not be identified by an authentic standard. These compounds were detected at m/z 471, 417, 313 (Figure 4).

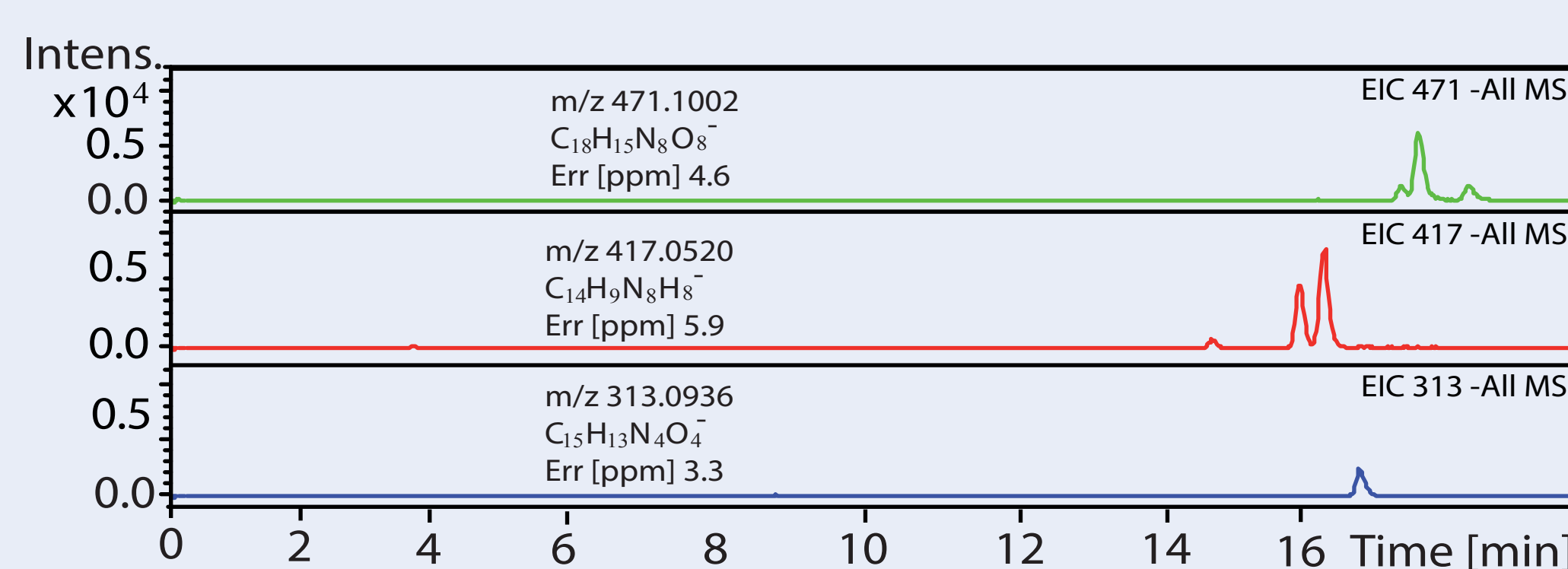


Figure 4: EIC of the oxidation products of 1,3,5-TMB which can not be identified with authentic standard compounds.

The DNPH derivatisation indicated that m/z 471 belongs to a C₆ compound with two carbonyl groups. Based on this the structure proposed by Healy et al., 2008 can be supported (cis/trans 2-methyl-4-oxopent-2-enal). The compound detected at m/z 417 was tentatively identified as glyoxal as it was found that this signal belongs to a C₂ compound with two carbonyl groups. Furthermore the formation of glyoxal during the 1,3,5-TMB oxidation was also suggested by Healy et al., 2008. Contrary, the m/z 313 compound was identified as a C₉ compound with one carbonyl group. This compound was also found by Metzger et al., 2008 which attributed m/z 313 to 3,5-dimethylbenzaldehyde.

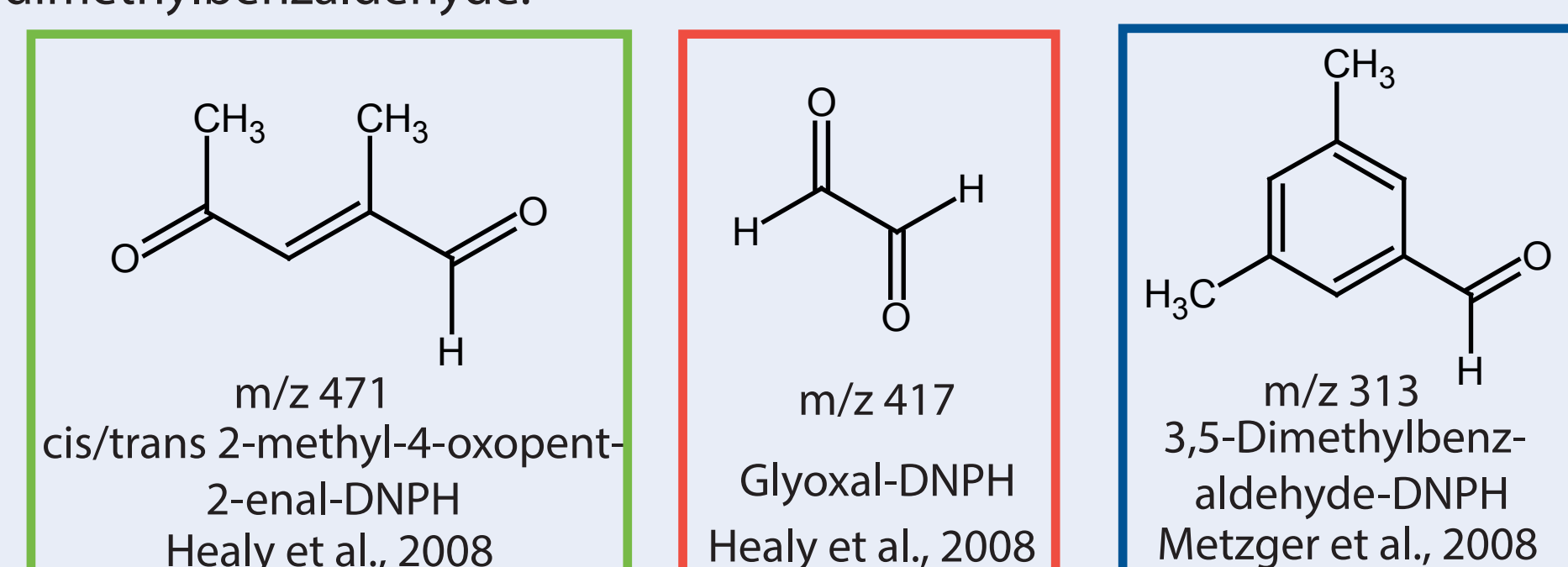


Figure 5: Suggested oxidation products of 1,3,5-TMB from literature studies.

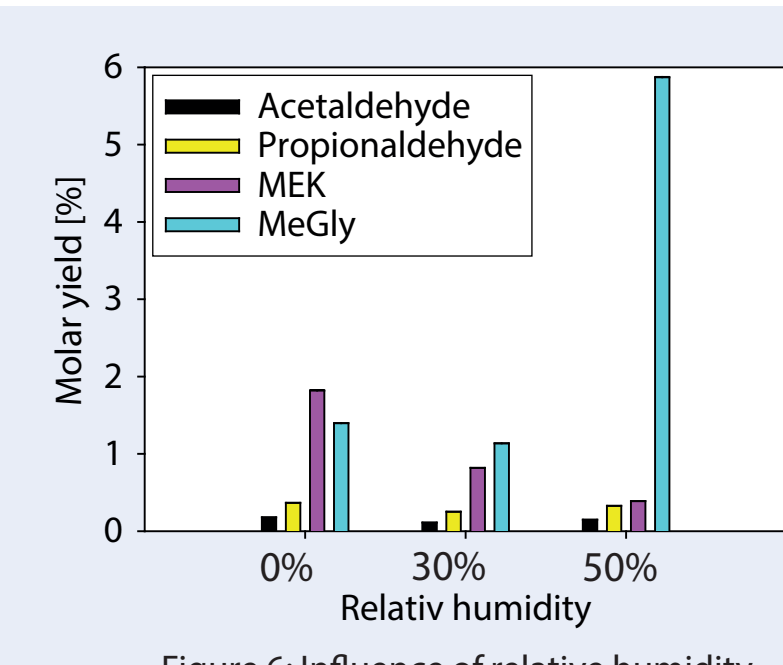


Figure 6: Influence of relative humidity

Influence of relative humidity

The product distribution of the particle phase products is strongly influenced by the RH. From Figure 6 it can be seen that MeGly showed the highest molar yield under elevated RH whereas MEK shows lower yields. This might indicate that MEK could act as a precursor compound for MeGly. Thus, MEK was oxidized in the aqueous phase to prove this hypothesis (Figure 7A/7B). Contrary, no influence of the RH was found on the molar yields of acetaldehyde and propionaldehyde indicating that the formation of these compounds is not affected by water and thus these compounds play no role for aqSOA formation.

Oxidation of MEK in the aqueous phase

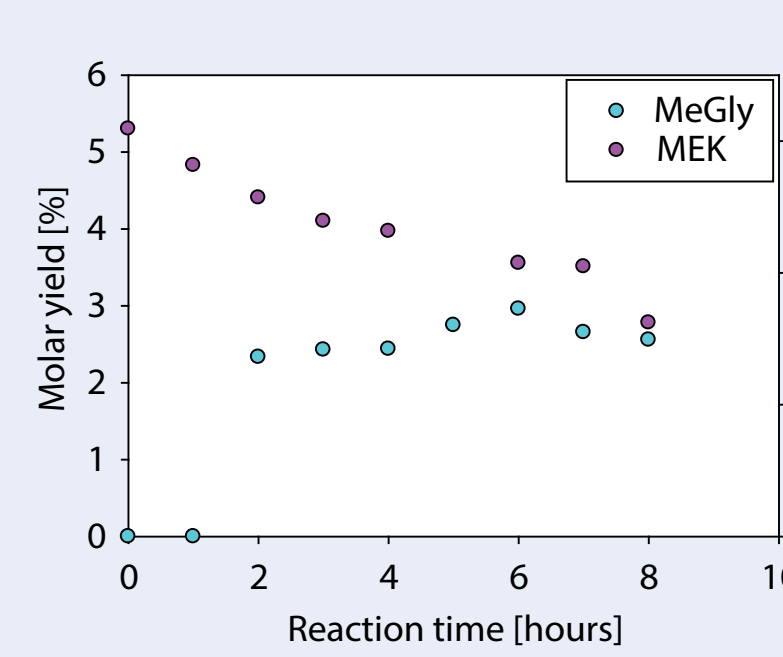


Figure 7A: Molar yield of MeGly during MEK oxidation.

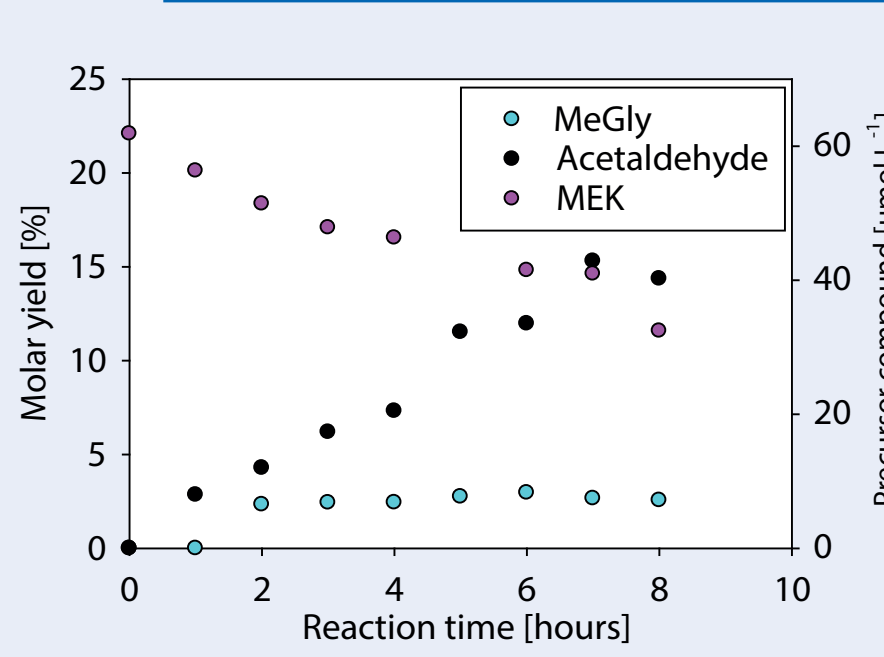


Figure 7B: Molar yield of MeGly and acetaldehyde during MEK oxidation.

MEK was oxidized in the bulk reactor (1 \times 10⁻⁴ mol L⁻¹) by OH radicals generated through the photolysis of hydrogen peroxide (1 \times 10⁻¹ mol L⁻¹). As it can be seen from Figure 7A considerable amounts of MeGly were formed. This observation supports the hypothesis that MEK is an aqSOA precursor for MeGly. Furthermore the curve shape of MeGly formation indicates that further reactions taking place. It is most likely that the further reaction of MeGly by OH radicals forms acetaldehyde, as it was also detected from bulk samples.

Simplified mechanism for the formation of MeGly

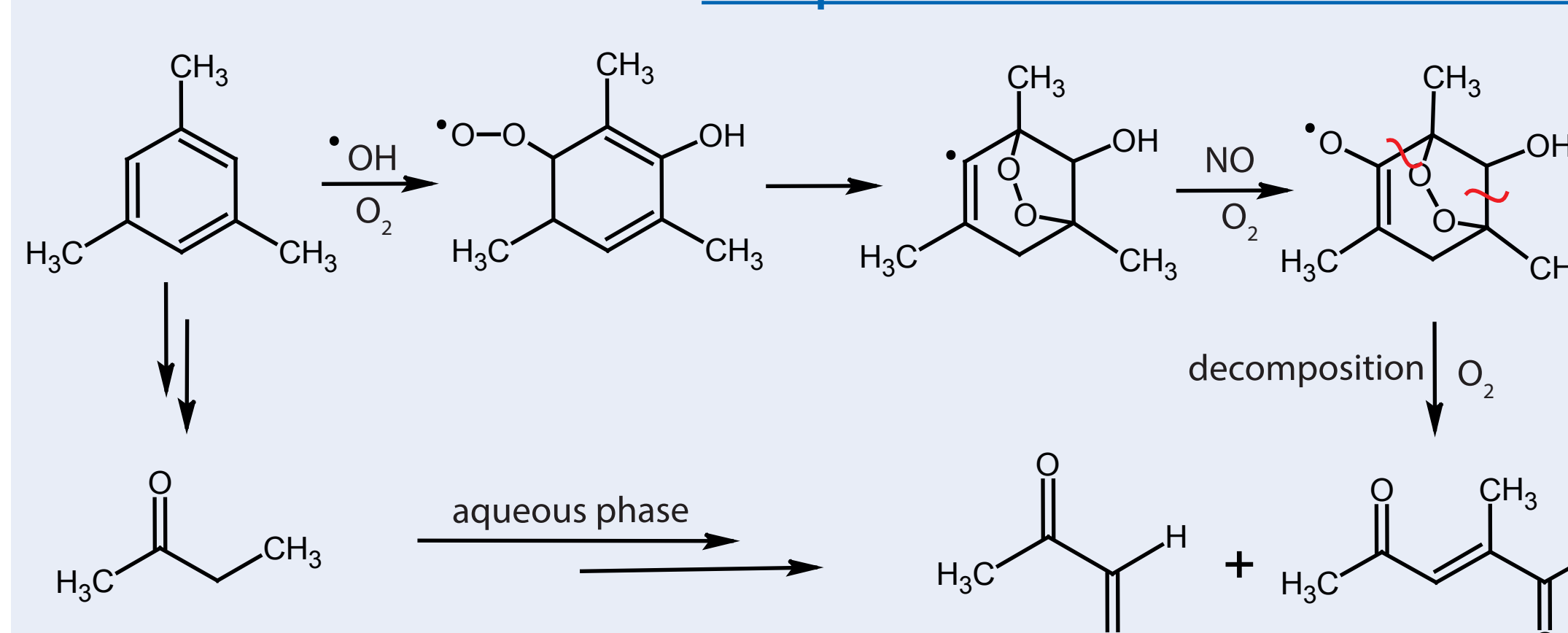


Figure 8: Simplified mechanism for the oxidation of 1,3,5-TMB to MeGly modified after Metzger et al., 2008.

The experimental data set can be summarized in a simplified mechanism. It is known that the oxidation of 1,3,5-TMB leads to the formation of cis/trans 2-methyl-4-oxopent-2-enal (m/z 471) and MeGly (Metzger et al., 2008) Furthermore it was found that MEK is formed as well which can react further within the particle phase forming MeGly. Consequently MEK is an aqSOA precursor compound for MeGly.

Conclusion

- SOA formed by the oxidation of 1,3,5-TMB is dominated by carbonyl compounds
 - RH influences the product distribution of the particle phase, especially of MEK and MeGly
 - MEK act as a precursor compound for MeGly
 - MeGly does also react further in the aqueous phase leading to the formation of acetaldehyde
- ➔ MEK and MeGly are important precursor compounds for aqSOA

Acknowledgement

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References

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