

Radical Driven Oxidation Processes of Isoprene Degradation Products in the Tropospheric Aqueous Phase

Tobias Otto, Bastian Stieger, Thomas Schaefer, Hartmut Herrmann

Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany

Member of the
TROPOS
Leibniz Institute for
Tropospheric Research

Member of the
Leibniz
Leibniz Association

Contact: tobias.otto@tropos.de

Motivation

Hydroxyl, nitrate and sulfate radicals are the most common oxidizing agents in the atmosphere besides the non-radical ones, ozone and hydrogen peroxide. These radicals contribute to atmospheric oxidation processes of organic compounds, such as Isoprene. Apart from methane, isoprene is the most emitted biogenic volatile organic compound (BVOC) with an annual emission of 594 ± 34 Tg.¹ methacrolein and methyl vinyl ketone are the first generation oxidation products of isoprene. Both of them are known to be water soluble. In detail, they undergo a reactive uptake.² Consequently, oxidation in the aqueous phase is

reasonable sink process of methacrolein, methyl vinyl ketone and even their oxidation products. The formed oxidation products contribute to the formation of aqueous secondary organic aerosol (aqSOA).³ Hence, kinetically and analytically investigations of these radical driven oxidation reactions of isoprene oxidation products in laboratory studies are necessary. The results can be implemented in atmospheric chemistry models, such as the Chemical aqueous phase radical mechanism (CAPRAM), as well as they will improve the prediction capability of the particle composition and consecutive the influence on the radiation balance.

Experimental

Isoprene Oxidation Products

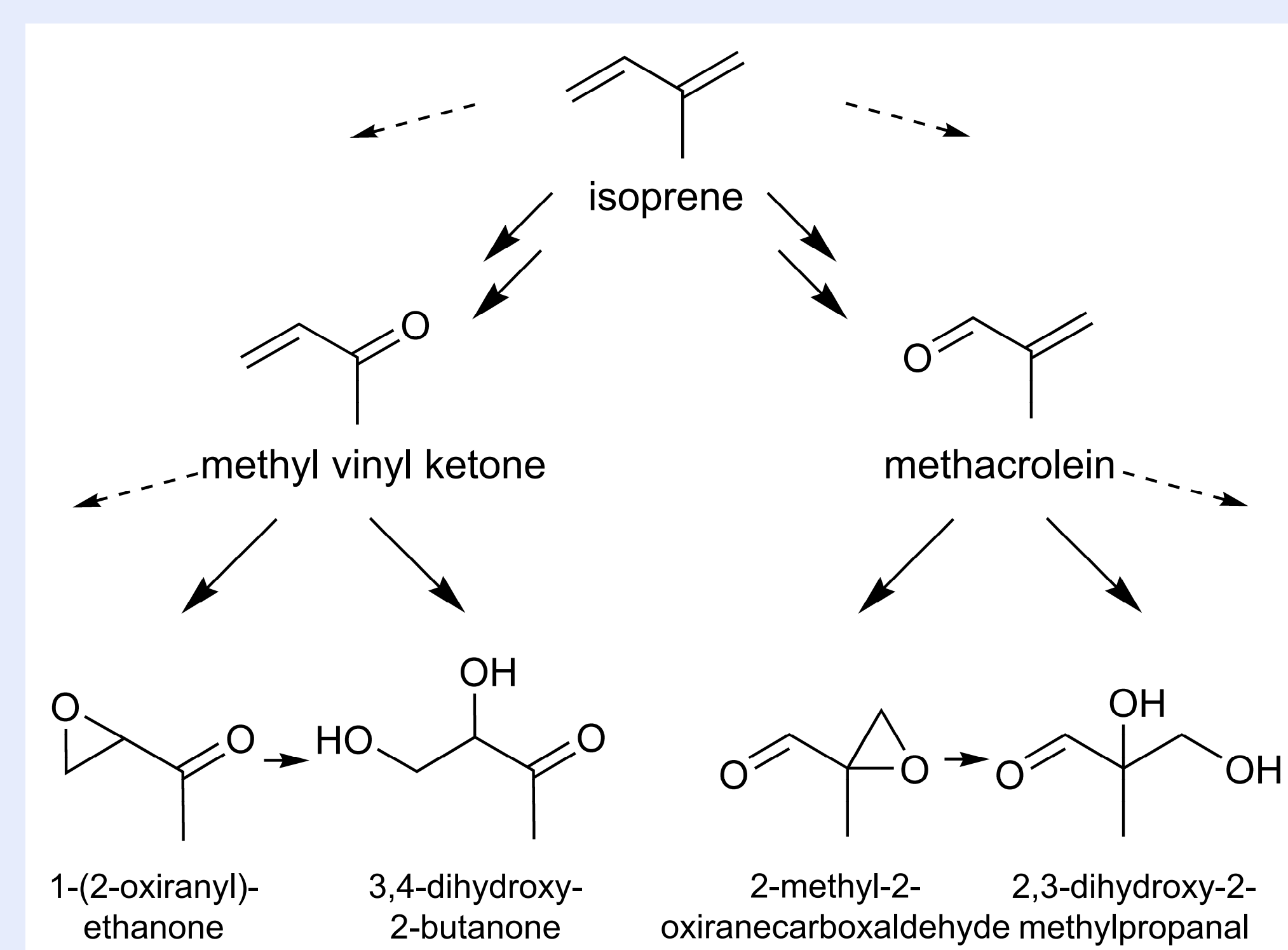


Figure 1: Investigated compounds and their origin

- Radical generation via photolysis of precursor compounds and subsequent reactions
- Organic reactant in a concentration range up to 5×10^{-4} M

Kinetics

- Laser Flash Photolysis – Long Path Absorption (LFP-LPA) setup
- Long path absorption by a White Mirror Cell⁴

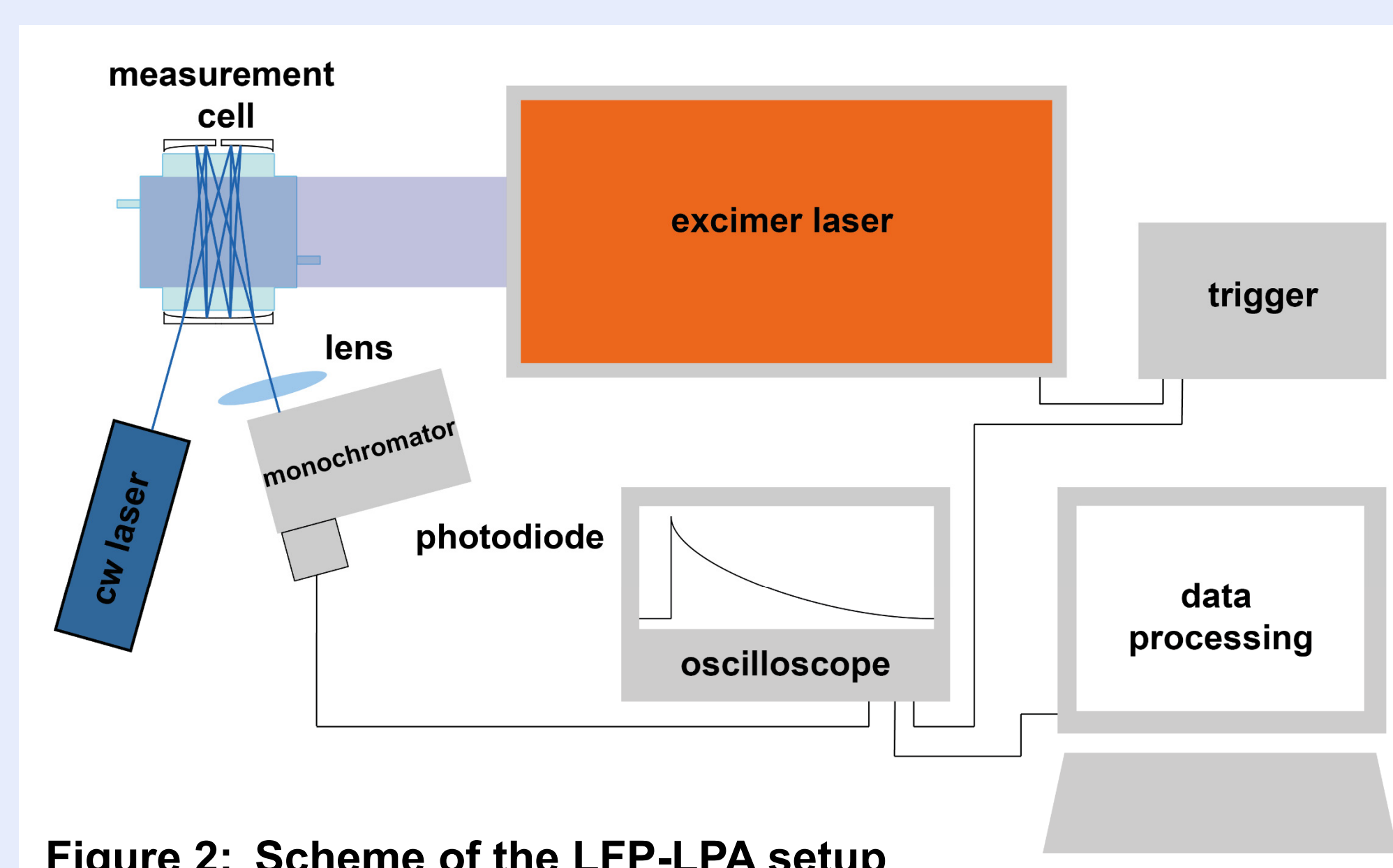


Figure 2: Scheme of the LFP-LPA setup

Table 1: Experimental conditions

radical	λ_{Photo} / nm	λ_{Obs} / nm	measurement specifications	precursors
hydroxyl radical (OH)	248	473	competition kinetics	$[\text{H}_2\text{O}_2] = 2 \times 10^{-4}$ M $[\text{SCN}^-] = 2 \times 10^{-5}$ M
sulfate radical (SO_4^-)	248	473	direct measurement	$[\text{S}_2\text{O}_8^{2-}] = 2.5 \times 10^{-4}$ M
nitrate radical (NO_3)	351	635	direct measurement	$[\text{S}_2\text{O}_8^{2-}] = 0.03$ M $[\text{NO}_3^-] = 0.1$ M

Product studies

- Product studies using a static irradiated photoreactor
- Irradiation by a Hg/Xe-lamp + bandpass filter ($\lambda = 254$ nm)
- Variable sampling intervals, common range 10 up to 30 min

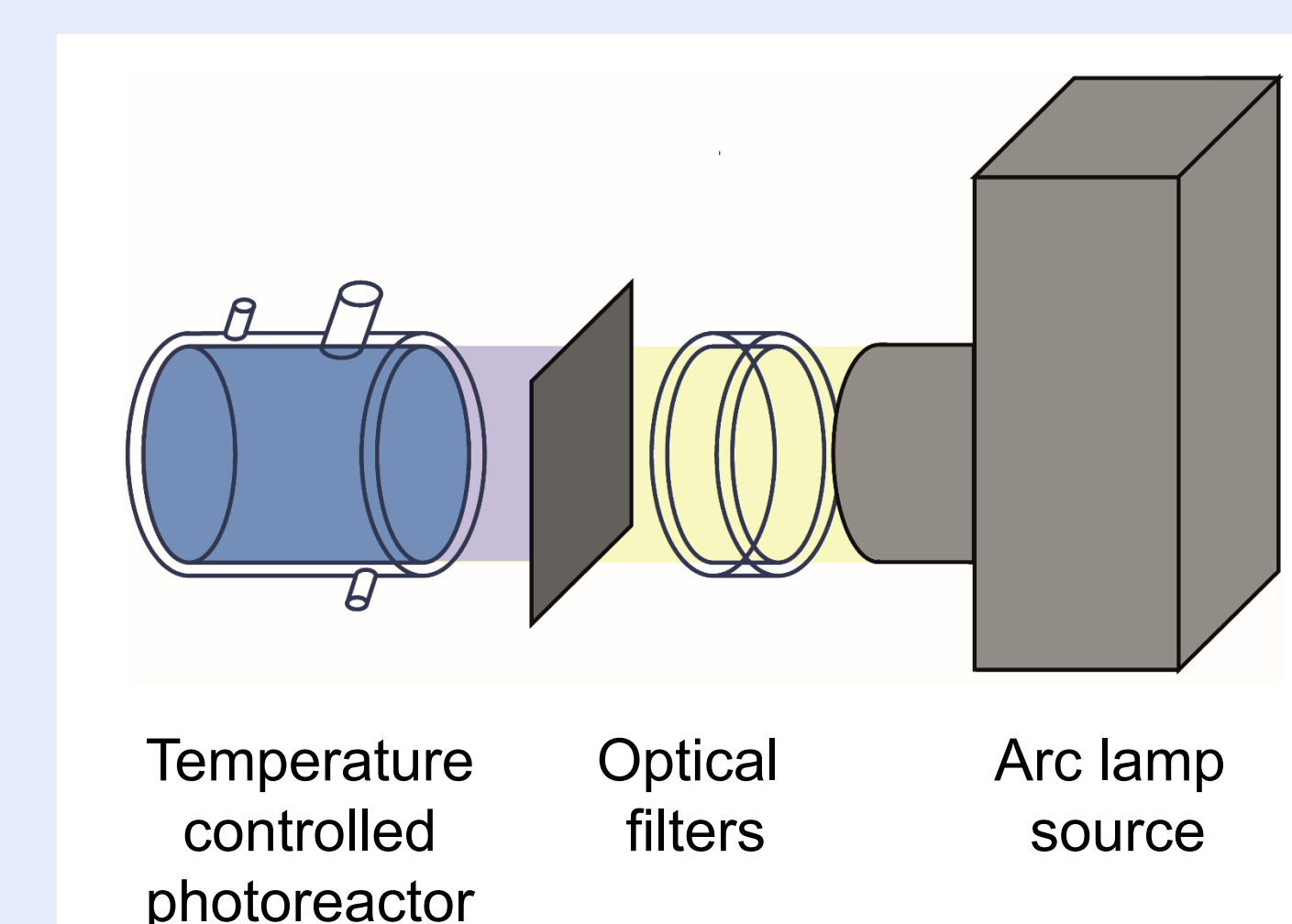


Figure 3: Scheme of the photoreactor setup

- Sample derivatisation with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) to analyse carbonyl group containing oxidation products
- Separation and detection via GC-MS

Results

Kinetics

- Kinetic investigation of the radical-driven oxidation reactions of the epoxides and diols of the first generation oxidation products of isoprene, methacrolein and methyl vinyl ketone, with OH, SO_4^- and NO_3 radicals in aqueous solution
- Determination of second order rate constants in a temperature range from 278 K to 318 K

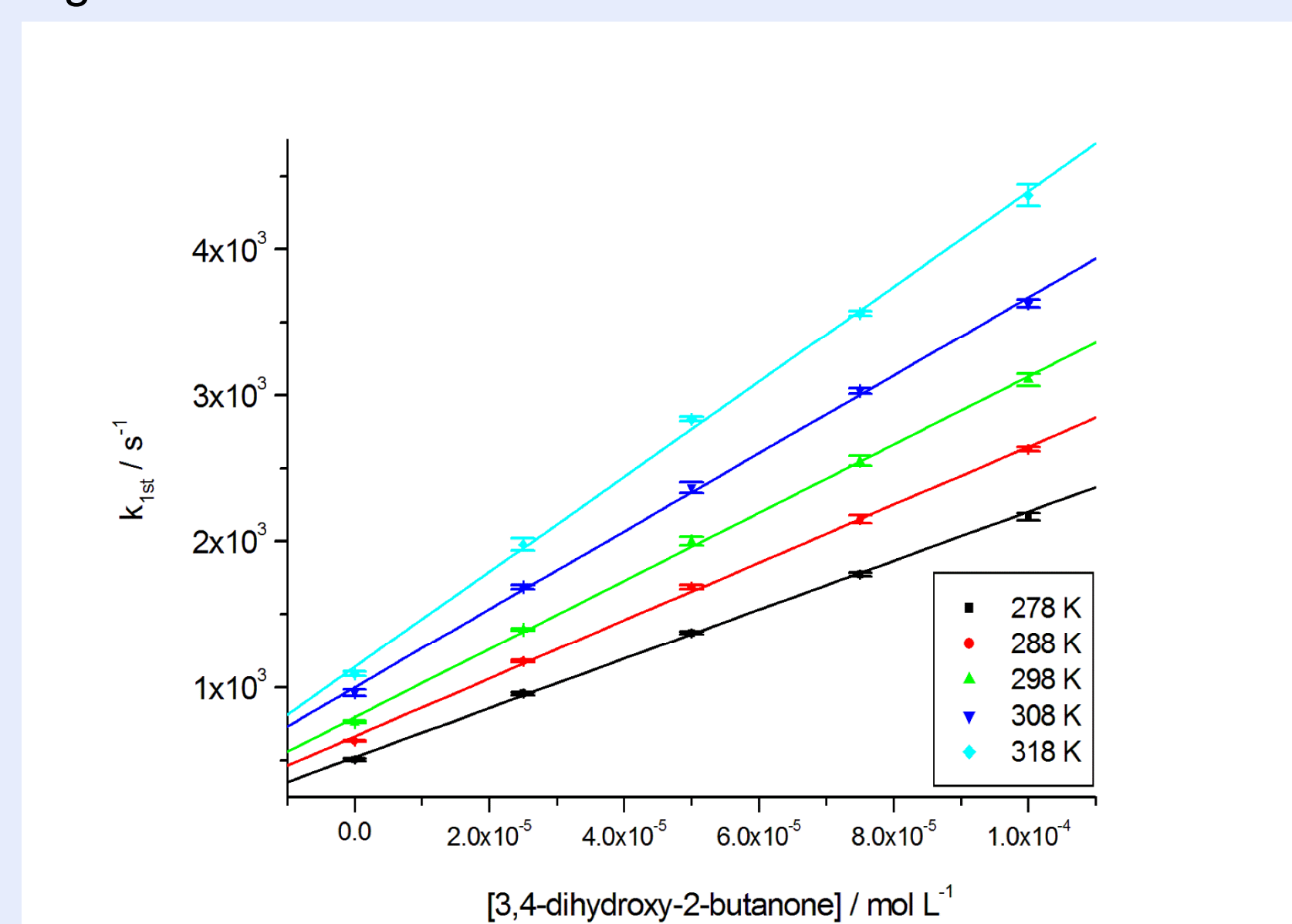


Figure 4: Temperature dependence of the reaction of OH radicals with 3,4-dihydroxy-2-butanone

- Reactivity of the epoxide of methyl vinyl ketone is in general lower as the one of the epoxide and the diol of methacrolein, due to weaker reaction sides

Table 2: Summary of the determined second order rate constants (T = 298 K)

compound	OH	NO_3	SO_4^-
		$k_{2\text{nd}} / 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$	
2-methyl-2-oxiranecarboxaldehyde	-	0.5 ± 0.1	2.3 ± 0.1
2,3-dihydroxy-2-methylpropanal	-	0.8 ± 0.1	3.3 ± 0.2
1-(2-oxiranyl)-ethanone	13.0 ± 4.0	-	0.7 ± 0.2
3,4-dihydroxy-2-butanone	99.0 ± 21.0	-	2.3 ± 0.1

- General order of reactivity: $\text{OH} > \text{SO}_4^- > \text{NO}_3$

Table 3: Corresponding activation parameters of the investigated reactions

compound	radical	A / $\text{L mol}^{-1} \text{ s}^{-1}$	E_A / kJ mol^{-1}
2-methyl-2-oxiranecarboxaldehyde	OH	-	-
	NO_3	$(1.6 \pm 0.3) \times 10^{12}$	31.5 ± 11.0
	SO_4^-	$(1.7 \pm 0.2) \times 10^9$	10.8 ± 7.0
2,3-dihydroxy-2-methylpropanal	OH	-	-
	NO_3	$(3.0 \pm 0.4) \times 10^{12}$	32.0 ± 9.1
	SO_4^-	$(2.4 \pm 0.2) \times 10^9$	10.5 ± 4.3
1-(2-oxiranyl)-ethanone	OH	$(5.0 \pm 0.3) \times 10^9$	9.0 ± 3.1
	NO_3	-	-
3,4-dihydroxy-2-butanone	SO_4^-	$(2.0 \pm 0.1) \times 10^7$	2.7 ± 1.3
	OH	$(4.1 \pm 0.8) \times 10^9$	3.6 ± 4.4
	NO_3	-	-
	SO_4^-	$(3.1 \pm 0.1) \times 10^9$	12.1 ± 1.6

Product studies

- Determination of carbonyl group containing reaction products of the reaction of methacrolein with OH radicals
- Main reaction products of the methacrolein oxidation: methylglyoxal, glycolaldehyde, hydroxyacetone
- Results in agreement with other studies³ using laser flash photolysis

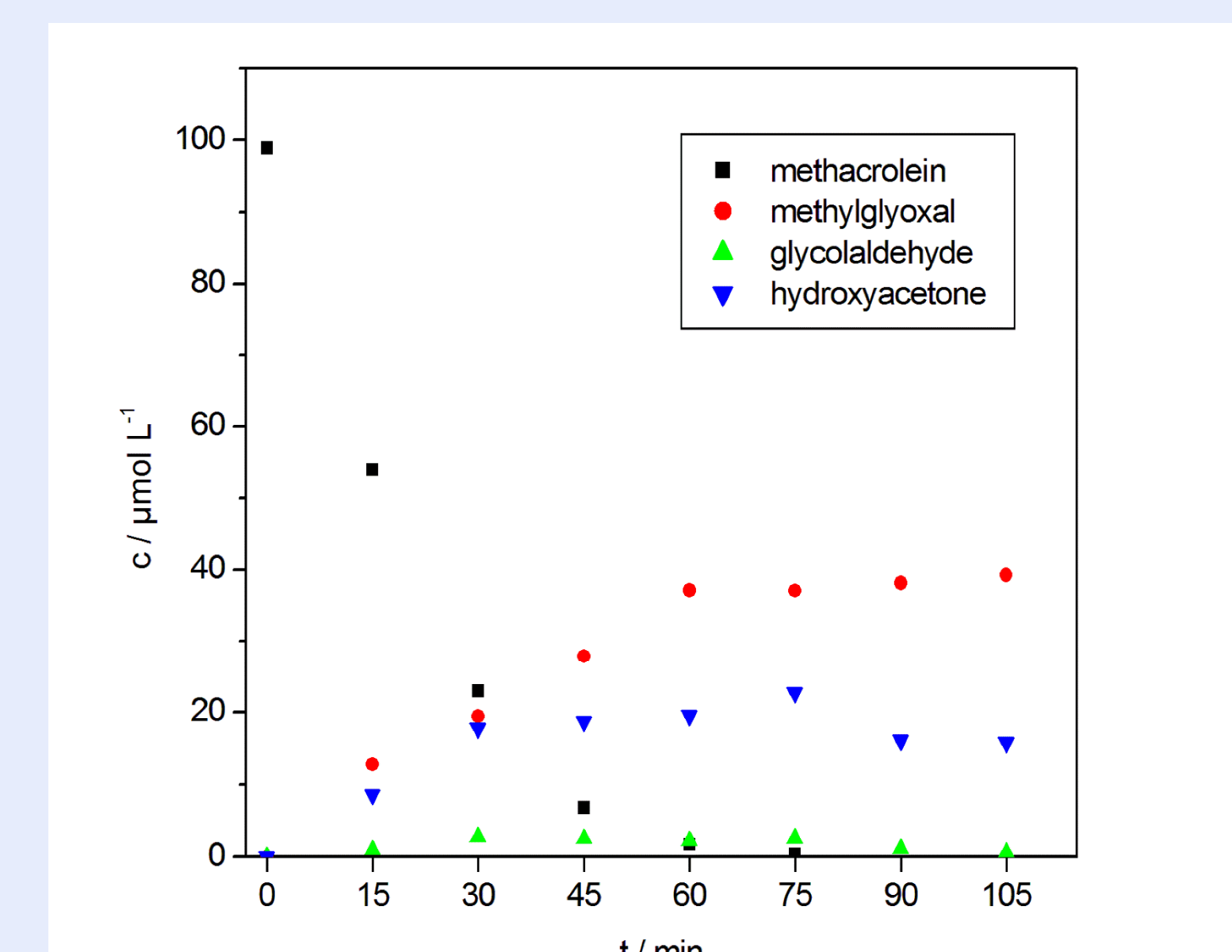


Figure 5: Concentration time profiles of the methacrolein oxidation

- Further identification of oxidation products using this method necessary

Outlook

- Further complementation of the atmospheric multiphase oxidation mechanism of isoprene and its degradation products, concerning the kinetic data of the epoxides and diols (summarized in Table 2 and 3)
- Studies of the isoprene oxidation products in the aqueous phase to enhance the understanding of the mechanism, identification of carboxylic acids using capillary electrophoresis
- Implementation of the obtained data in CAPRAM

Acknowledgement

This work was done in the framework of the MISOX 2 project (grant number HE 3086/13-1) funded by the DFG (German Research Foundation).

References

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