Atmospheric oxidation processes of Isoprene degradation products in aqueous solution

Tobias Otto, Bastian Stieger, Thomas Schaefer, Hartmut Herrmann

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

Contact: tobias.otto@tropos.de

TROPOS
Leibniz Institute for
Tropospheric Research

Member of the
Leibniz Association

Motivation

Free radicals, such as hydroxyl and nitrate radicals, are common atmospheric oxidizing agents, which contribute to atmospheric oxidation processes of organic compounds. Isoprene is the most emitted biogenic volatile organic compound (BVOC) apart from methane, with a source strength from 500 – 750 Tg a^{-1}).[1] The first generation degradation products methacrolein and methyl vinyl ketone are the first oxidation products, which are known to be water soluble. In detail, they undergo a reactive uptake.[2] Therefore, degradation reactions in the aqueous phase are reasonable sink processes of these compounds and their formed oxidation products contribute to the formation of aqueous secondary organic aerosol.[3] Hence, radical driven oxidation reactions of isoprene degradation products have to be kinetically and analytically investigated in laboratory studies. The results of these studies can be implemented in multiphase models, such as CAPRAM, as well as they will improve the prediction capability of the particle composition and consecutive the radiation balance.

Experimental

- Kinetic studies by using a Laser Flash Photolysis – Long Path Absorption (LFP-LPA) setup
- Long path absorption by a White Mirror Cell[4]
- Radical generation via photolysis of precursor compounds or subsequent reactions

Table 1: Experimental conditions

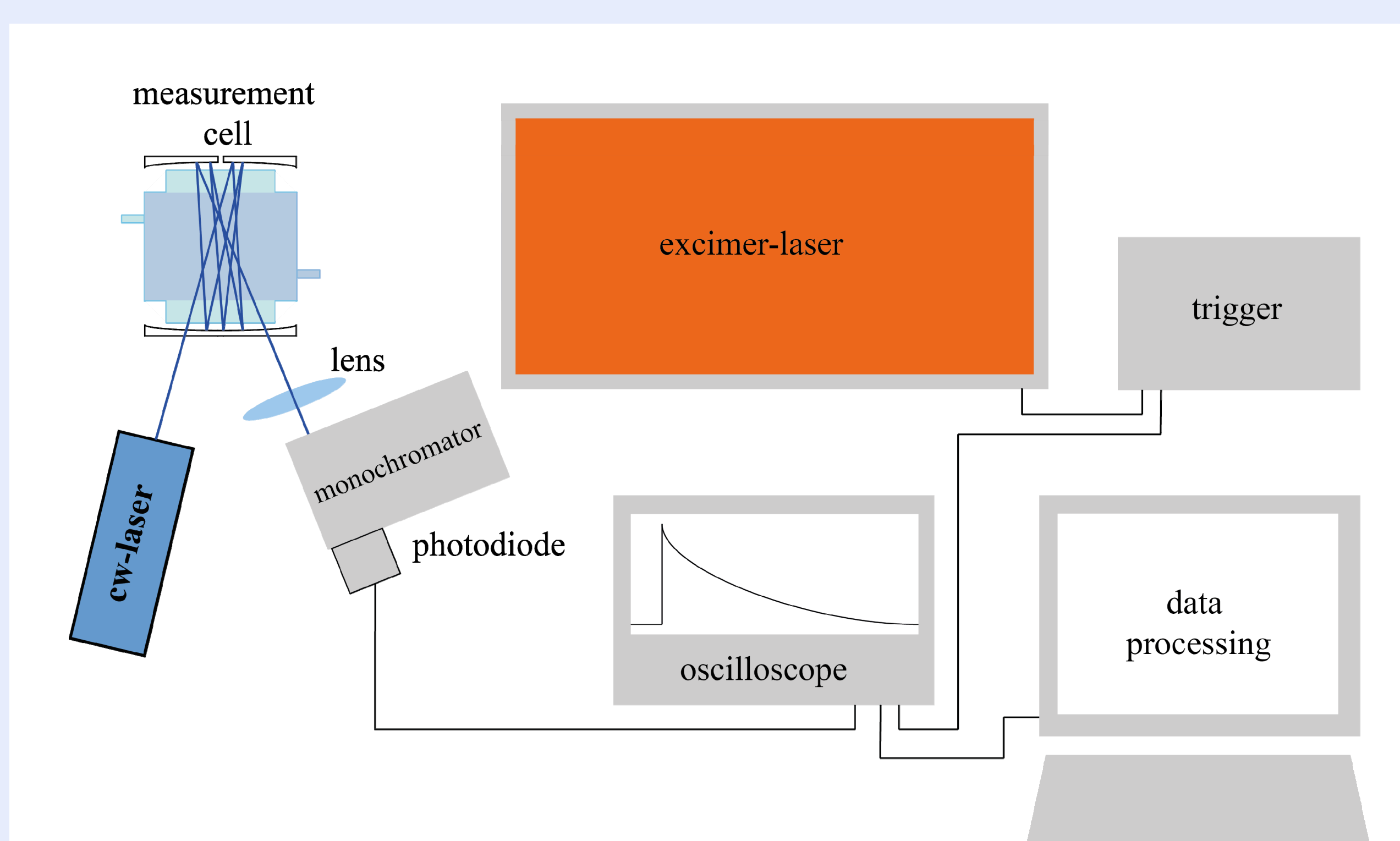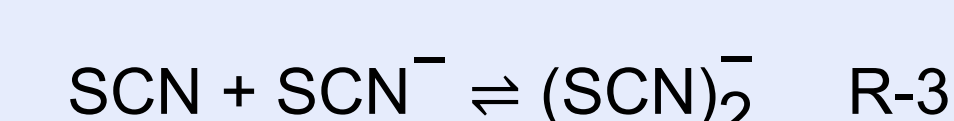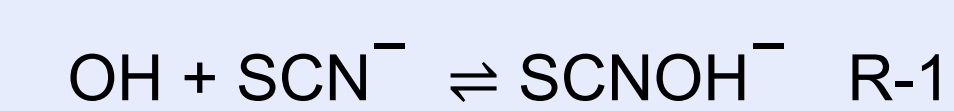| radical	λ_{Photo} / nm	λ_{Obs} / nm	measurement specifications	precursors
hydroxyl radical (OH)	248	473	competition kinetics	$[H_2O_2] = 2 \times 10^{-4}$ M $[SCN^-] = 2 \times 10^{-5}$ M
sulfate radical (SO_4^-)	248	473	direct measurement	$[S_2O_8^{2-}] = 2.5 \times 10^{-4}$ M
nitrate radical (NO_3)	351	635	direct measurement	$[S_2O_8^{2-}] = 0.03$ M $[NO_3^-] = 0.1$ M

Figure 1: Scheme of the LFP-LPA setup

- Organic reactant in a concentration range up to 5×10^{-4} M
- Direct observation of the decay of the formed radicals, in case of SO_4^- and NO_3
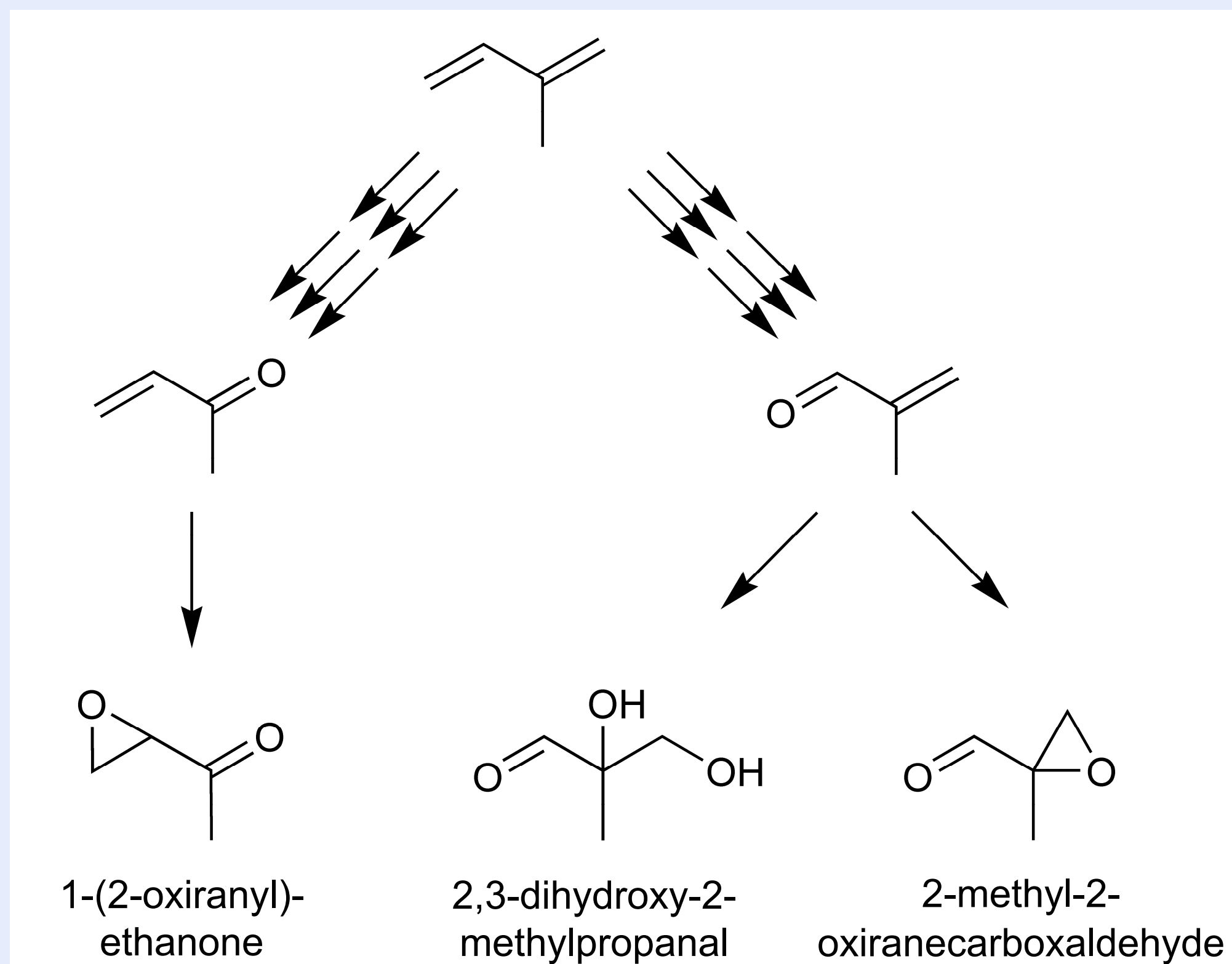- Observation of the competing reactant system (R-1 – R-3), in the case of the hydroxyl radical:

$$OH + SCN^- \rightleftharpoons SCNOH^- \quad R\text{-}1$$

$$SCNOH^- \rightleftharpoons OH^- + SCN \quad R\text{-}2$$

$$SCN + SCN^- \rightleftharpoons (SCN)_2^- \quad R\text{-}3$$

Results

Figure 2: Kinetically investigated compounds and their origin

1-(2-oxiranyl)-ethanone

2,3-dihydroxy-2-methylpropanal

2-methyl-2-oxiranecarboxaldehyde

- 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
- OH reaction rate constants superior to SO_4^- and NO_3
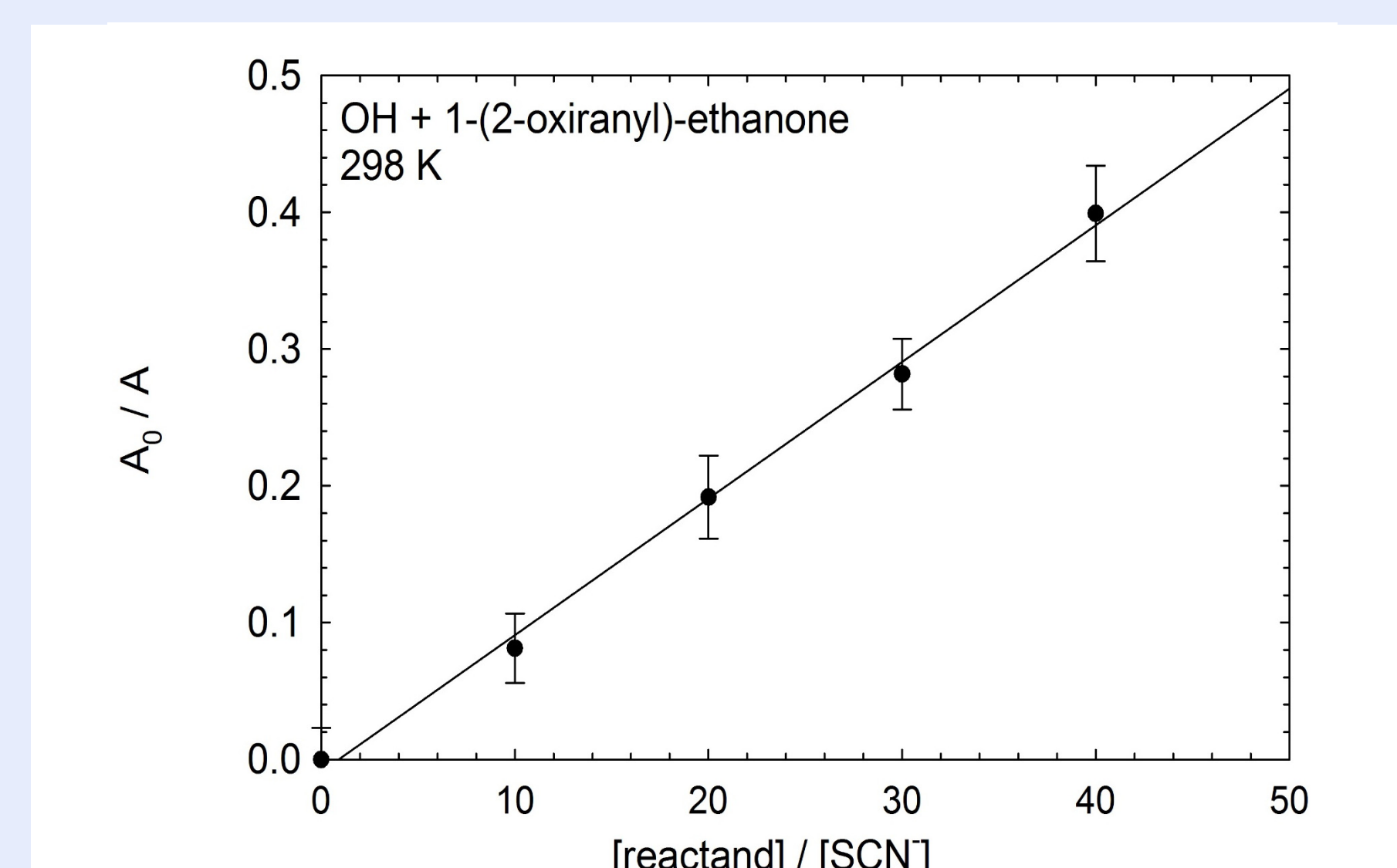- General order of reactivity: OH > SO_4^- > NO_3

Figure 3: Determination of k_{2nd} by plotting the ratio of the absorptions against the ratio of the concentrations of the reactant and the rhodanide reference
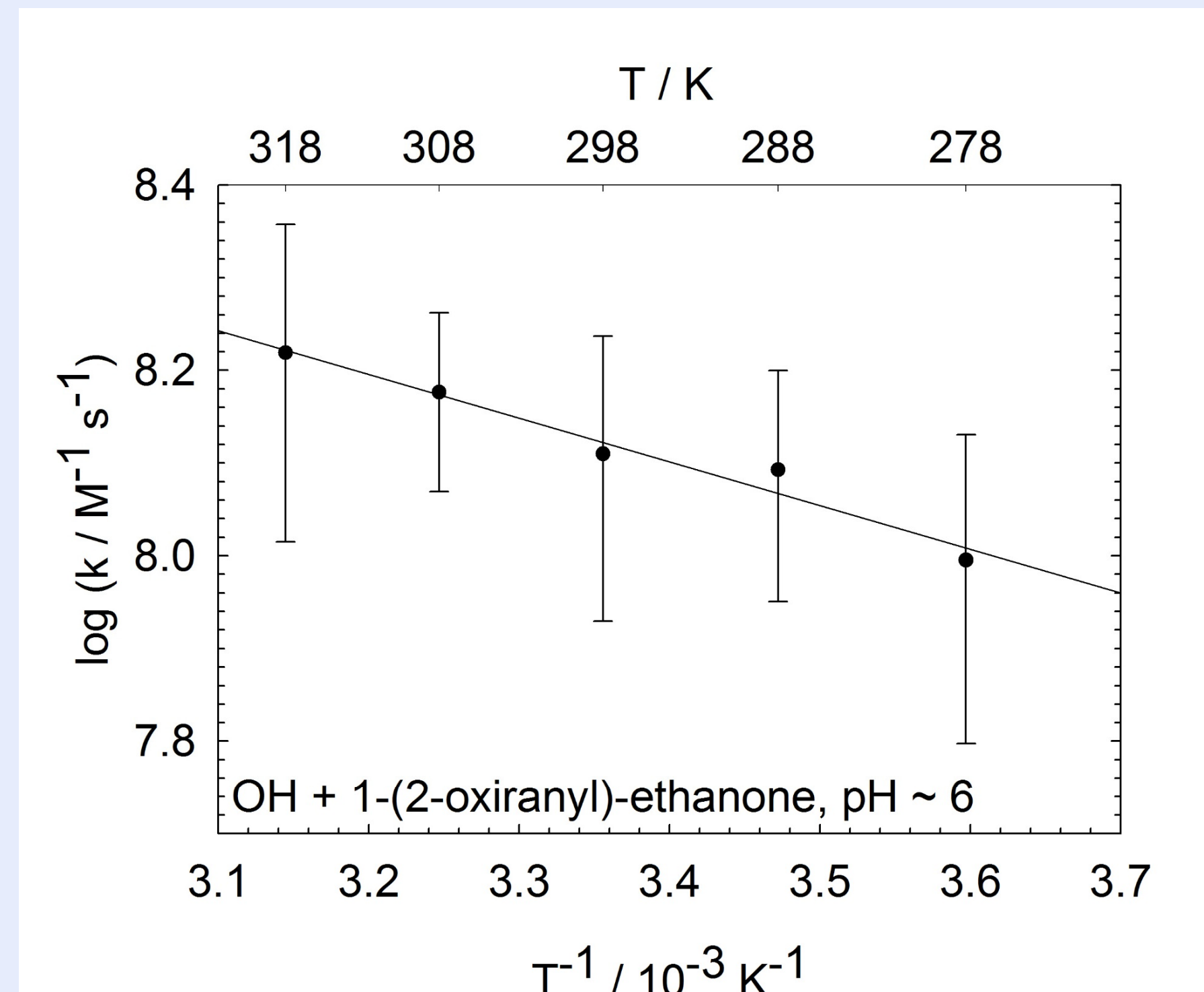

Figure 4: Temperature dependency of the reaction of OH radicals with 1-(2-oxiranyl)-ethanone at pH ~ 6

- 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 k_{2nd} / L mol^{-1} s^{-1}	NO_3 k_{2nd} / L mol^{-1} s^{-1}	SO_4^- k_{2nd} / L mol^{-1} s^{-1}
2-methyl-2-oxiranecarboxaldehyde	-	$(4.76 \pm 1.09) \times 10^6$	$(2.31 \pm 0.10) \times 10^7$
2,3-dihydroxy-2-methylpropanal	-	$(7.94 \pm 0.60) \times 10^6$	$(3.25 \pm 0.15) \times 10^7$
1-(2-oxiranyl)-ethanone	$(1.29 \pm 0.44) \times 10^8$	-	$(6.90 \pm 1.99) \times 10^6$

Table 3: Calculated activation parameters of the investigated reactions

compound	radical	A / L mol^{-1} s^{-1}	E_A / kJ mol^{-1}	$\Delta G^\ddagger$ / kJ mol^{-1}	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}
2-methyl-2-oxiranecarboxaldehyde	OH	-	-	-	-	-
	NO_3	-	-	-	-	-
	SO_4^-	$(1.7 \pm 0.2) \times 10^9$	10.8 ± 7.0	31.2 ± 24.3	8.4 ± 5.4	$(-76.5) \pm 10.2$
2,3-dihydroxy-2-methylpropanal	OH	-	-	-	-	-
	NO_3	$(3.0 \pm 0.4) \times 10^{12}$	32.0 ± 9.1	33.8 ± 13.9	29.5 ± 8.4	$(-14.3) \pm 1.8$
	SO_4^-	$(2.4 \pm 0.2) \times 10^9$	10.5 ± 4.3	30.0 ± 14.8	8.0 ± 3.3	$(-73.8) \pm 6.0$
1-(2-oxiranyl)-ethanone	OH	$(5.0 \pm 0.3) \times 10^9$	9.0 ± 3.1	26.7 ± 10.7	6.5 ± 2.3	$(-67.5) \pm 3.8$
	NO_3	-	-	-	-	-
	SO_4^-	$(2.0 \pm 0.1) \times 10^7$	2.7 ± 1.3	34.0 ± 17.8	0.2 ± 0.1	$(-113.4) \pm 3.6$

Note: for the first activation table row the first compound was listed as "2-methyl-2-oxiranecarboxaldehyde" with OH and an entry $(1.6 \pm 0.3) \times 10^{12}$, 31.5 ± 11.0, 34.9 ± 17.7, 29.0 ± 10.1, $(-19.36) \pm 3.1$

Summary & 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)
- Expansion of the kinetic investigations regarding the missing data and 3,4-dihydroxy-2-butanone, the diol derivative of methyl vinyl ketone
- Product studies of the oxidation products of the kinetically investigated compounds in the aqueous phase to enhance the understanding of the mechanism
- Implementation of the obtained data in CAPRAM

Acknowledgement

References

1) Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P. I.; Geron, C. *Atmos. Chem. Phys.* **2006**, *6*, 3181-3210.
2) Liu, Z.; Wu, L. Y.; Wang, T. H.; Ge, M. F.; Wang, W. G. *J. Phys. Chem. A* **2012**, *116*, 437-442.
3) Schöne, L.; Schindelka, J.; Szeremeta, E.; Schaefer, T.; Hoffmann, D.; Rudzinski, K. J.; Szmigielski, R.; Herrmann, H. *Phys. Chem. Chem. Phys.*, **2014**, *16*, 6257-6272.
4) White, J. U. *J. Opt. Soc. Am.* **1942**, *32*, 285.