Laboratory studies on the reactivity of atmospherically relevant poly-alcohols towards radicals in aqueous phase

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Motivation

⚐ Levoglucosan ($C_6H_{10}O_5$) and other polyolic compounds such as Erythritol ($C_4H_{10}O_4$), Arabitol ($C_5H_{12}O_5$) and Mannitol ($C_6H_{14}O_6$) can represent an important fraction of the water soluble organic carbon (WSOC) in atmospheric particles influenced by natural emissions or biomass burning [1,3]. Due to their source specifity, polyols and in particular levoglucosan are applied as tracer compounds for source apportionment studies.

⚐ Only few studies investigated the atmospheric stability and degradation products of these very polar and water soluble compounds. The stability of levoglucosan towards acid-catalyzed hydrolysis ([2]; no degradation over 10 days) and the decomposition in presence of ambient oxidants and sunlight ([3]; no degradation within 8 hours) was studied. Furthermore, Holmes et al., 2007 [4] showed the formation of oligomeric compounds after the oxidation of levoglucosan in presence of OH radicals. However, the reactivity of these compounds towards atmospheric radicals was not yet systematically characterized and considered in lifetime calculations.

⚐ Using the laser-photolysis-long-path-absorption (LP-LPA) technique, the kinetics of OH, NO_3 and SO_4^- radical reactions with levoglucosan, erythritol, arabitol and mannitol in aqueous solution were studied as a function of the temperature. The kinetic data obtained will be used to better evaluate the atmospheric stability of the investigated compounds.
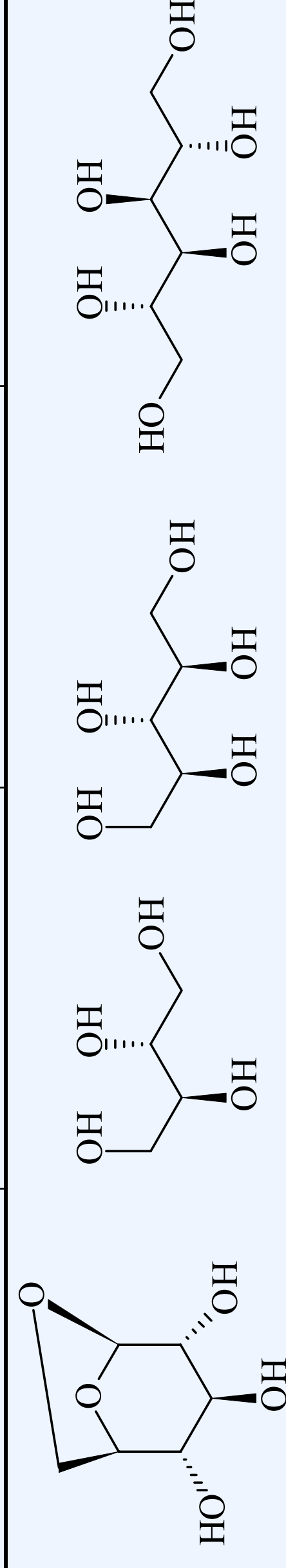
Experimental

NO_3 radical

$S_2O_8^{2-} + h\nu$ (λ=248 nm) $\longrightarrow$ 2 SO_4^-
$NO_3^- + SO_4^-$ $\longrightarrow$ $NO_3 + SO_4^{2-}$

Detection wavelength: λ = 635 nm

SO_4^- radical

$S_2O_8^{2-} + h\nu$ (λ=248 nm) $\longrightarrow$ 2 SO_4^-

Detection wavelength: λ = 473 nm

OH radical

$H_2O_2 + h\nu$ (λ=248 nm) $\longrightarrow$ 2 OH
OH + SCN$^-$ $\rightleftharpoons$ SCNOH$^-$
SCNOH$^-$ $\rightleftharpoons$ SCN$^-$ + OH$^-$
SCN$^-$ + SCN$^-$ $\rightleftharpoons$ (SCN)$_2^-$

Detection wavelength: λ = 473 nm

Fig. 1: Thermostated laser flash photolysis – long path absorption setup applied for the kinetic investigation.

Results and discussion

Table 1: Bond dissociation energies (BDE), Henry coefficients (H), second order rate constants (T = 298 K) and activation parameter obtained for the investigated radical reaction in aqueous solution.

Radical	Compound	k_{2nd} [M^{-1}s^{-1}] T = 298K	Literature [M^{-1}s^{-1}]	BDE* kJ/mol	H M/atm	E_A [kJ/mol]	A [M^{-1}s^{-1}]	$\Delta H^\ddagger$ [kJ/mol]	$\Delta G^\ddagger$ [kJ/mol]	$\Delta S^\ddagger$ [J/K mol]
OH	Levoglucosan	(2.4 ± 0.3) · 10^9	-	-	-	9.0 ± 2.9	(8.7 ± 0.4) · 10^{10}	6.5 ± 2.1	19.6 ± 7.3	-(43.8 ± 2.1)
	Erythritol	(1.9 ± 0.2) · 10^9	1.5 · 10^9 [5]	379.5	2 · 10^{16}	16.2 ± 1.8	(1.3 ± 0.04) · 10^{12}	13.7 ± 1.5	20.0 ± 2.7	-(21.1 ± 0.6)
	Arabitol	(1.6 ± 0.2) · 10^9	1.8 · 10^9 [5]	379.4	9 · 10^{20}	6.6 ± 3.5	(2.5 ± 0.1) · 10^{10}	4.2 ± 2.2	20.3 ± 11.9	-(54.1 ± 3.2)
	Mannitol	(1.6 ± 0.3) · 10^9	1.7 · 10^9 [6]	379.3	4 · 10^{25}	6.1 ± 1.8	(1.8 ± 0.1) · 10^{10}	3.6 ± 1.1	20.5 ± 6.7	-(56.7 ± 1.7)
NO_3	Levoglucosan	(1.6 ± 0.2) · 10^7	-			17.8 ± 2.6	(2.3 ± 0.1) · 10^{10}	15.4 ± 2.2	31.7 ± 5.9	-(54.9 ± 2.4)
	Erythritol	(1.4 ± 0.2) · 10^7	-			19.3 ± 3.4	(3.4 ± 0.2) · 10^{10}	16.9 ± 3.0	32.3 ± 7.6	-(51.7 ± 2.9)
	Arabitol	(1.5 ± 0.3) · 10^7	-			16.6 ± 3.6	(1.1 ± 0.1) · 10^{10}	14.1 ± 3.1	32.2 ± 9.1	-(60.7 ± 3.8)
	Mannitol	(1.4 ± 0.2) · 10^7	-			20.5 ± 6.6	(5.1 ± 0.6) · 10^{10}	18.0 ± 5.8	32.4 ± 13.9	-(48.2 ± 5.2)
SO_4^-	Levoglucosan	(5.2 ± 0.8) · 10^7	-			9.0 ± 3.0	(2.1 ± 0.1) · 10^9	6.6 ± 2.2	28.9 ± 11.4	-(74.8 ± 4.3)
	Erythritol	(4.2 ± 0.3) · 10^7	-			4.5 ± 1.6	(2.6 ± 0.1) · 10^8	2.1 ± 0.7	29.5 ± 11.3	-(91.9 ± 3.1)
	Arabitol	(5.3 ± 1.0) · 10^7	-			16.5 ± 5.4	(3.9 ± 0.4) · 10^{10}	14.0 ± 4.6	29.1 ± 12.1	-(50.6 ± 4.6)
	Mannitol	(5.0 ± 0.7) · 10^7	-			14.4 ± 4.4	(1.6 ± 0.1) · 10^{10}	11.9 ± 3.7	29.3 ± 11.3	-(58.1 ± 4.5)

* bond dissociation energies were calculated using Benson incremental method [7]

⚐ Good comparison of the OH rate constants obtained with literature data from pulse radiolysis studies. For the other radicals no literature values available.

⚐ OH radicals show the highest reactivity towards the investigated compounds.

Reactivity order: OH >> SO_4^- > NO_3

⚐ No effect of the chain length on the rate constants obtained.

Levoglucosan $C_6H_{10}O_5$

Erythritol $C_4H_{10}O_4$

Arabitol $C_5H_{12}O_5$

Mannitol $C_6H_{14}O_6$

Fig. 3 (left): Plot of log(k_{2nd}) vs. BDE for different OH radical reactions. ● this work; ◄ other OH reactions, see Gaillard et al., 2007 [8]

Fig. 4 (right): Plot of log(k_{2nd}) vs. BDE for different NO_3 radical reactions. ● this work; ◄ other NO_3 reactions, see Gaillard et al., 2007 [8]

Fig. 2: Summary of the measured Arrhenius plots for the investigated radical reactions in aqueous solution.
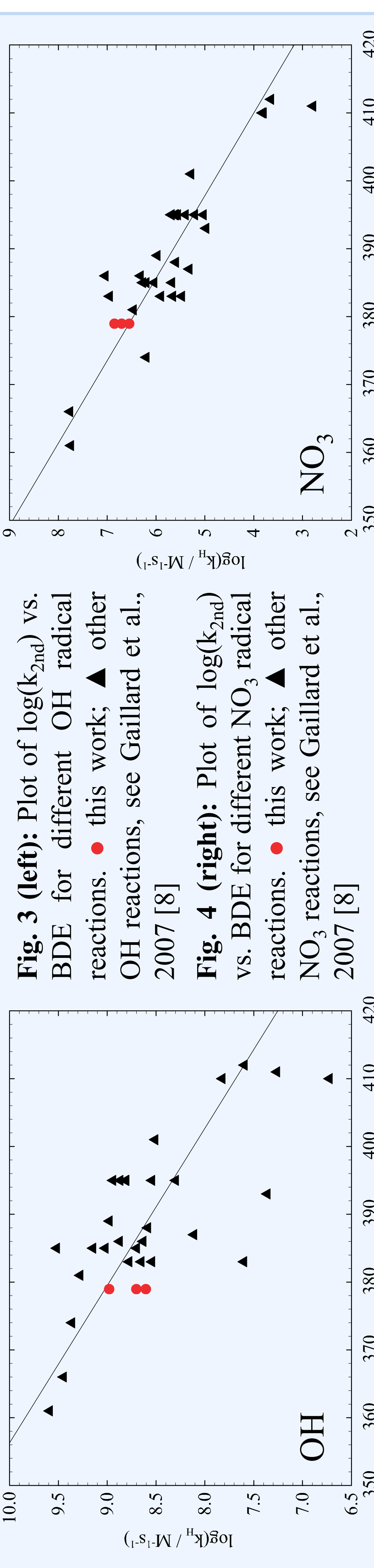
⚐ Obtained OH and NO_3 rate constants correlate well with the calculated bond dissociation energies of the reactants.

Table 2: Calculated tropospheric lifetimes (in hours) in deliquescent particles for the investigated compounds under remote and polluted (urban) conditions. Radical concentrations were taken from CAPRAM 3.0i [9].

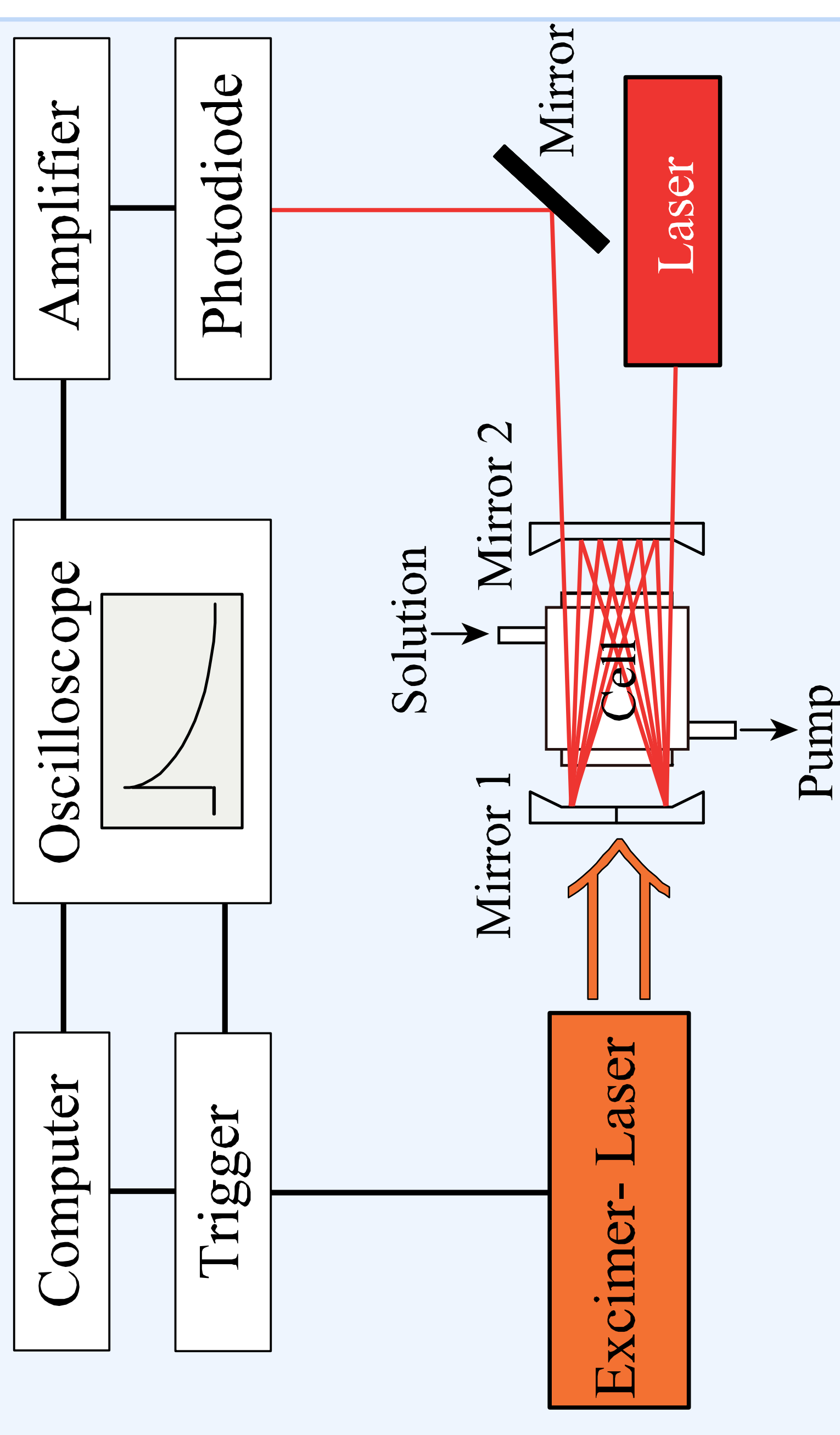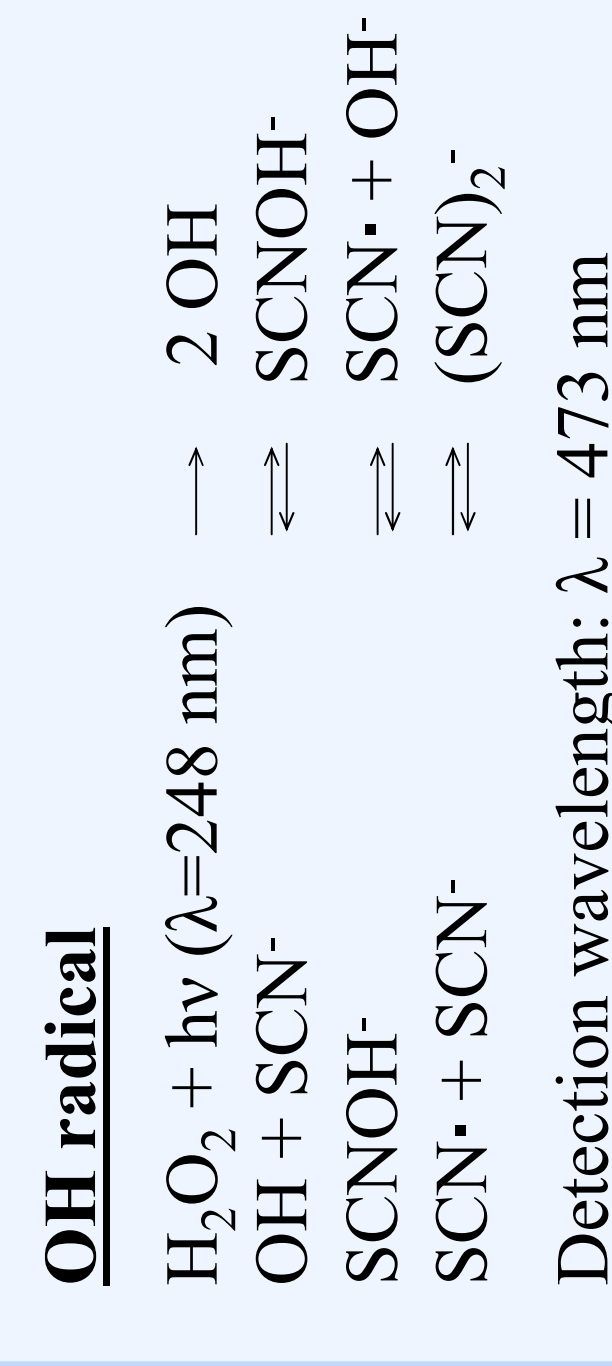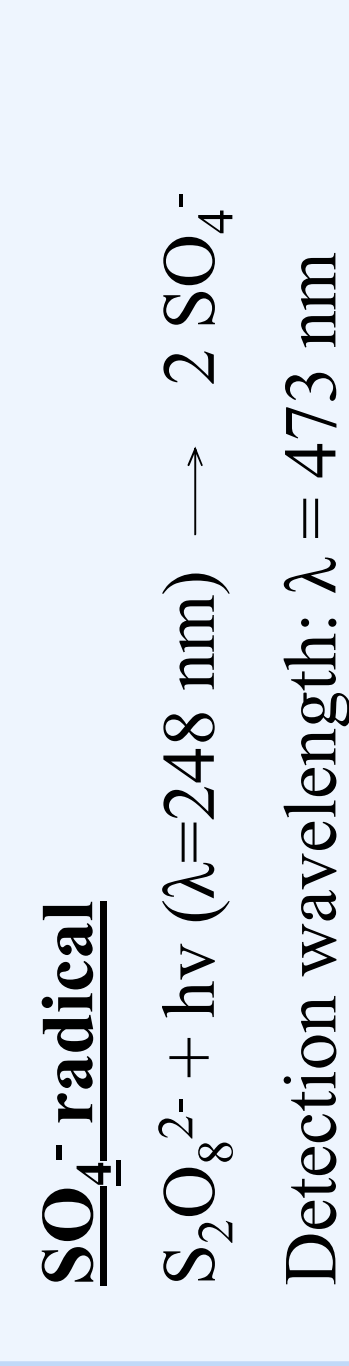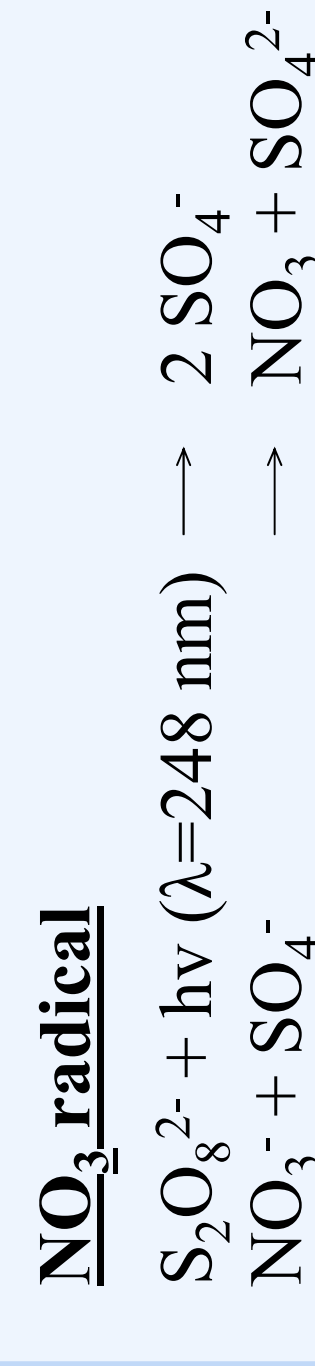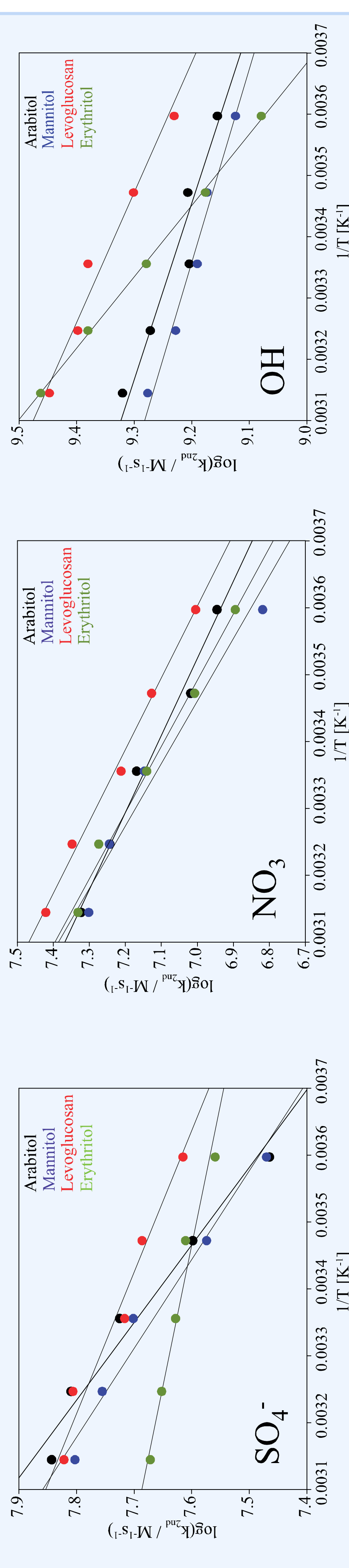| Compound	Tropospheric lifetimes τ [h]							
	OH 3.7·10^{-12} M	OH 7.3·10^{-13} M	NO_3 7.0·10^{-13} M	NO_3 2.0·10^{-13} M	SO_4^- 5.3·10^{-13} M	SO_4^- 6.0·10^{-15} M		
	remote	urban	remote	urban	remote	urban		
Levoglucosan	0.03	0.16	24.8	86.8	10.1	890.3		
Erythritol	0.04	0.20	28.3	99.2	12.5	1102.3		
Arabitol	0.05	0.24	26.5	92.6	9.9	873.5		
Mannitol	0.05	0.24	28.3	99.2	10.5	925.9		

Conclusions and Outlook

⚐ Calculated tropospheric lifetimes (Table 2) for the investigated OH radical reactions are less than one hour. Comparison of the calculated lifetimes with other available lifetimes for levoglucosan in the literature indicates that radical reactions in aqueous solution could be the most important sink process for these compounds, if the mass transfer in the aqueous phase is not the rate determining step. Therefore, the atmospheric stability, in particular for levoglucosan as an important tracer compound, should be carefully re-evaluated in modelling studies considering also aqueous phase radical chemistry.

⚐ Further investigation on the product distribution of the studied radical reactions will be carried out.

References

[1] K.E.Yttri et al., *Atmos. Chem. Phys.*, **2007**, 7, 4267-4279.
[2] M.P. Fraser and K. Lakshmanan, *Environ. Sci. Technol.*, **2000**, 34, 4560-4564.
[3] B.R.T. Simoneit; *Appl. Geochem.*, **2002**, 17, 129-162.
[4] J. Holmes and G.A. Petrucci, *J. Atmos. Chem.*, **2007**, 58, 151-166.
[5] J.S. Moore et al., Radiation Biology and Chemistry. Research Developments, H.E. Edwards (ed.), Elsevier, New York, **1979**.
[6] G.V. Buxton et al., *J. Phys. Chem. Ref. Data*, **1988**, 17, 813-886.
[7] S. W. Benson, Thermochemical Kinetics, Wiley, New York, 2nd edn., **1976**.
[8] P. Gaillard et al., *Phys. Chem. Chem. Phys.*, **2007**, 9, 958-968.
[9] http://projects.tropos.de/capram/