

Fate of Isoprene-derived Dihydroxycarbonyl Compounds in the Tropospheric Aqueous Phase

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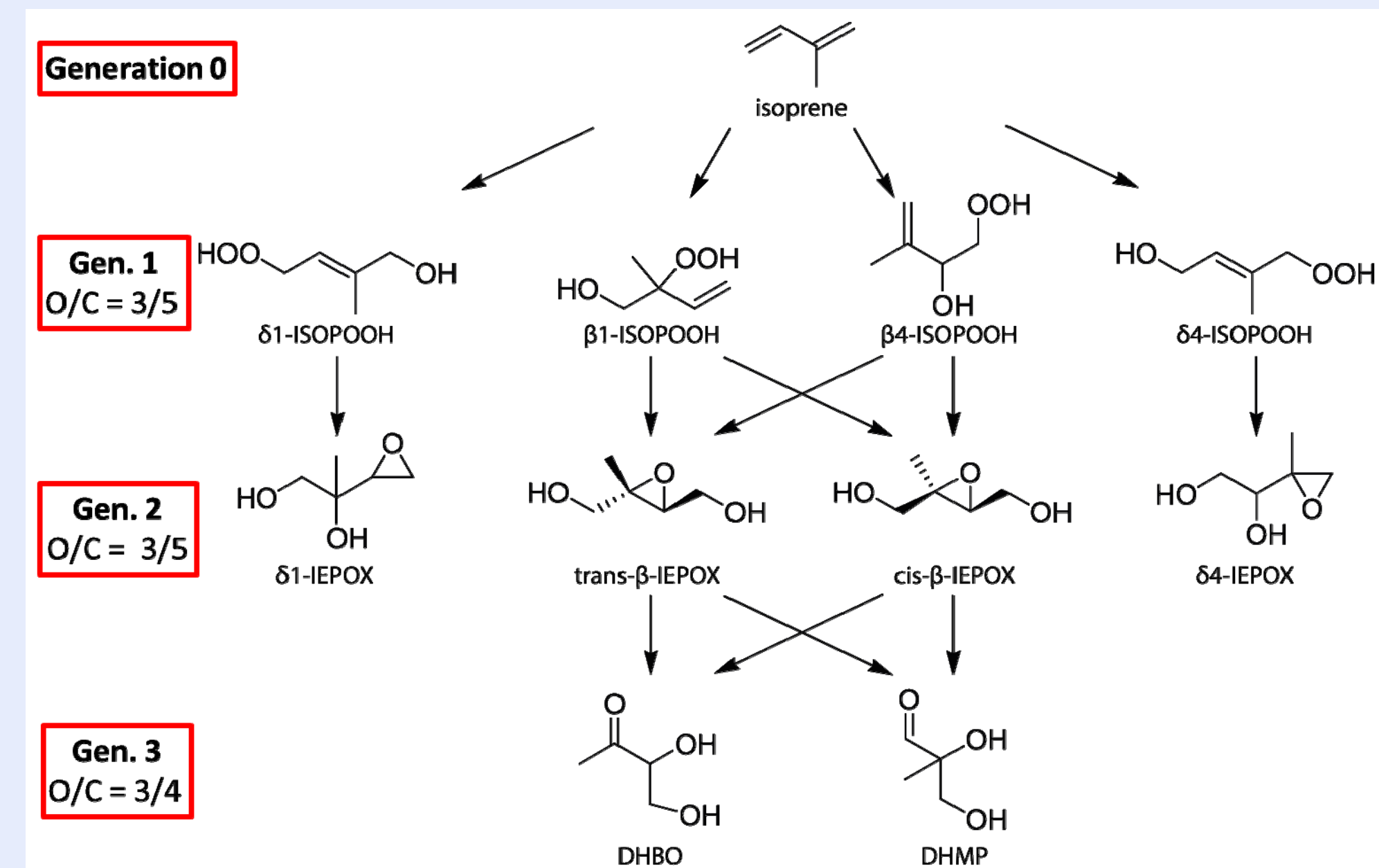
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Motivation

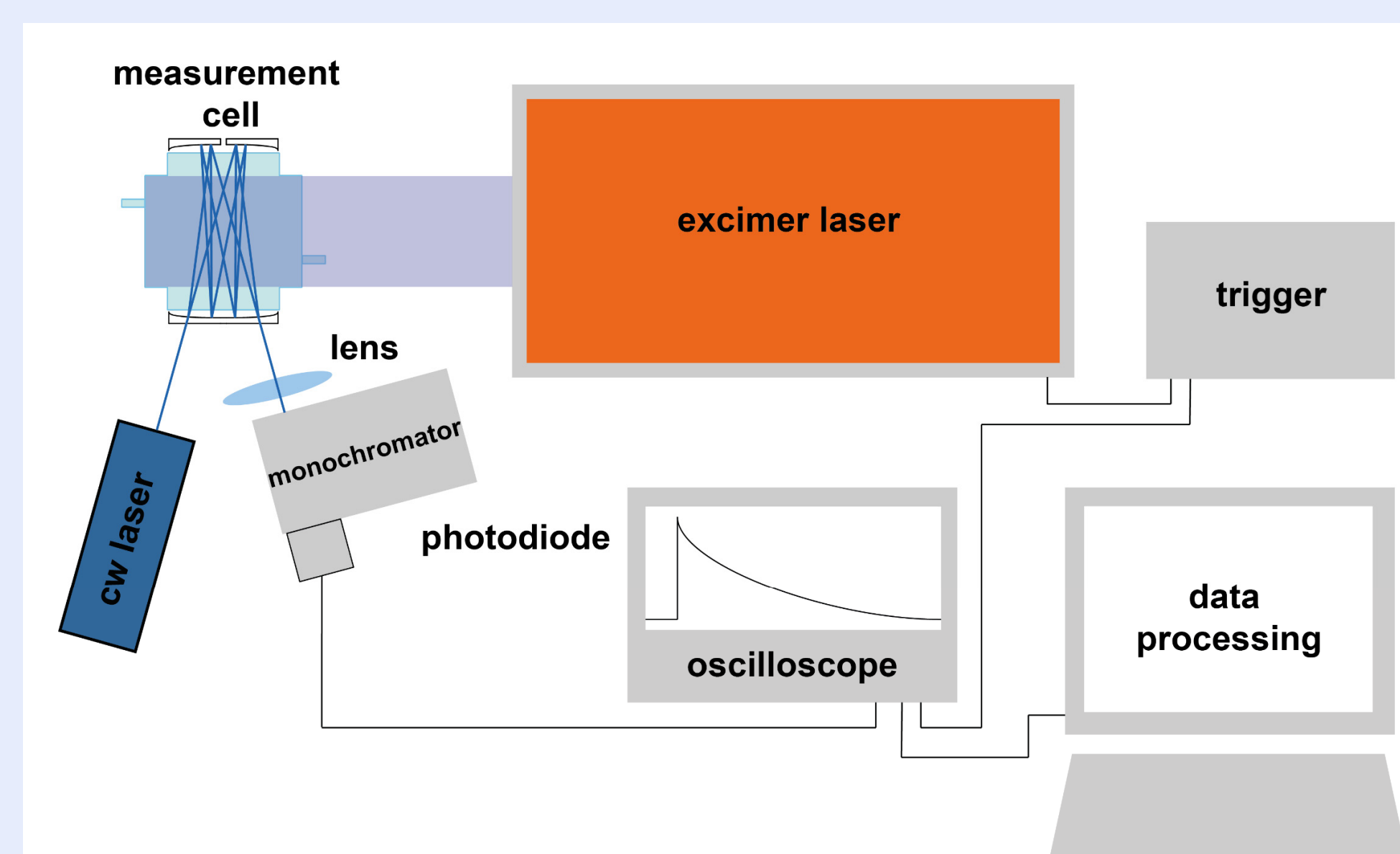
Isoprene is the most emitted biogenic volatile organic compound (BVOC) with an annual emission of $594 \pm 34 \text{ Tg C yr}^{-1}$. $\text{C}_4\text{H}_8\text{O}_3$ dihydroxycarbonyl compounds, such as DHBO and DHMP, are the 3rd generation oxidation products of isoprene under HO_x -dominated, low NO_x conditions. The global annual production rate of all C_4 dihydroxycarbonyl compounds is estimated to be 54 Tg C yr^{-1} .² Their predicted Henry's law constants let suppose that DHBO and DHMP effectively partition to the tropospheric aqueous phase. Hence, kinetic and analytical investigations of radical-driven oxidation reactions of these isoprene oxidation products in laboratory studies are necessary to clarify the aqueous-phase oxidation mechanism and the impact of a changing ionic strength and matrix composition.



Experimental

Kinetics

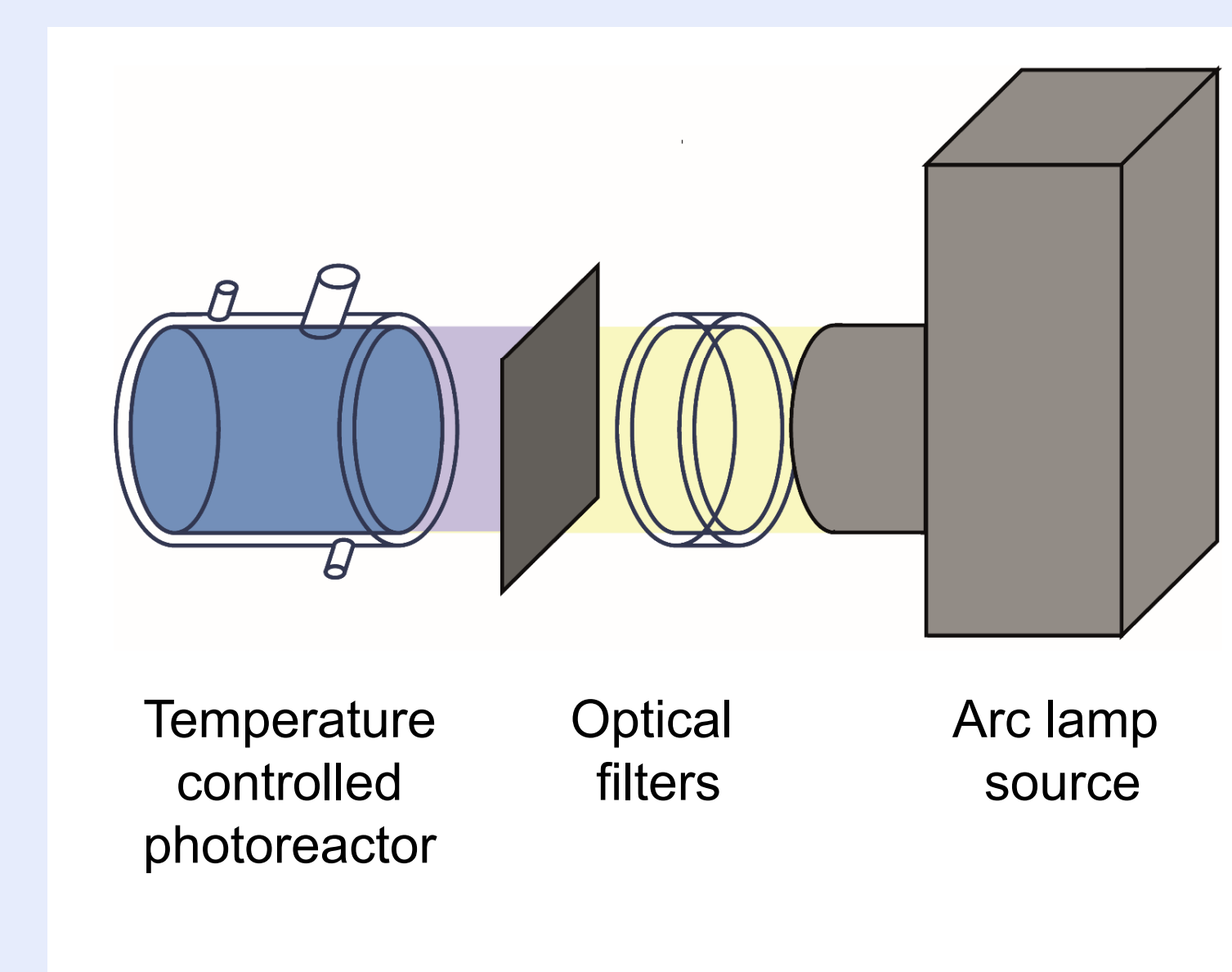
- Laser Flash Photolysis – Long Path Absorption (LFP-LPA) setup
- Long path absorption by a White Mirror Cell³



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

Product studies

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



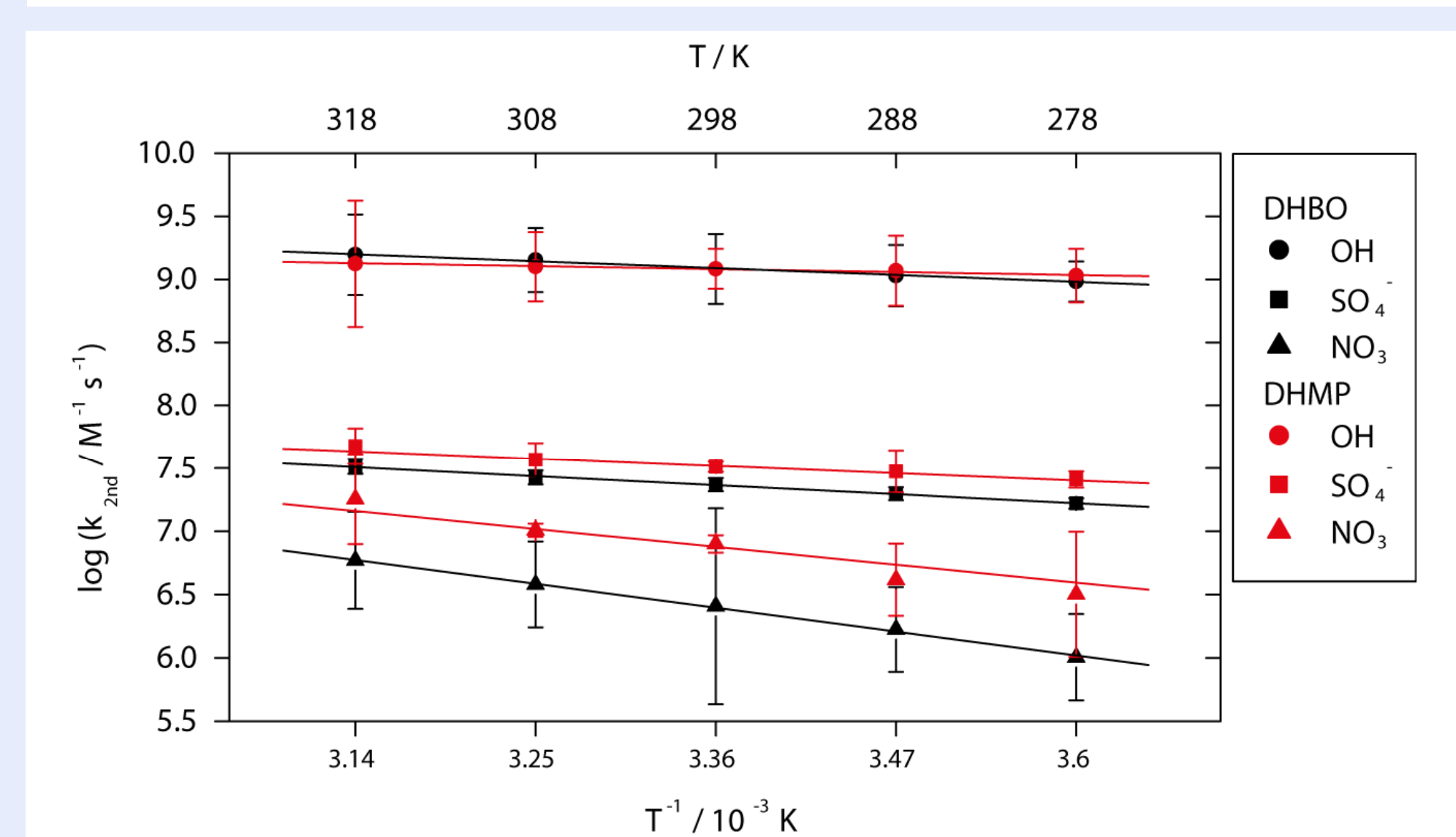
- precursor concentrations of $200 \mu\text{M}$ / L hydrogenperoxide and $100 \mu\text{M}$ / L organic substrate
- Sample derivatization with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) to analyze carbonyl group containing oxidation products via GC-MS⁴
- Analysis of smaller C_2 to C_4 acids via CE-UV

Results

Kinetics

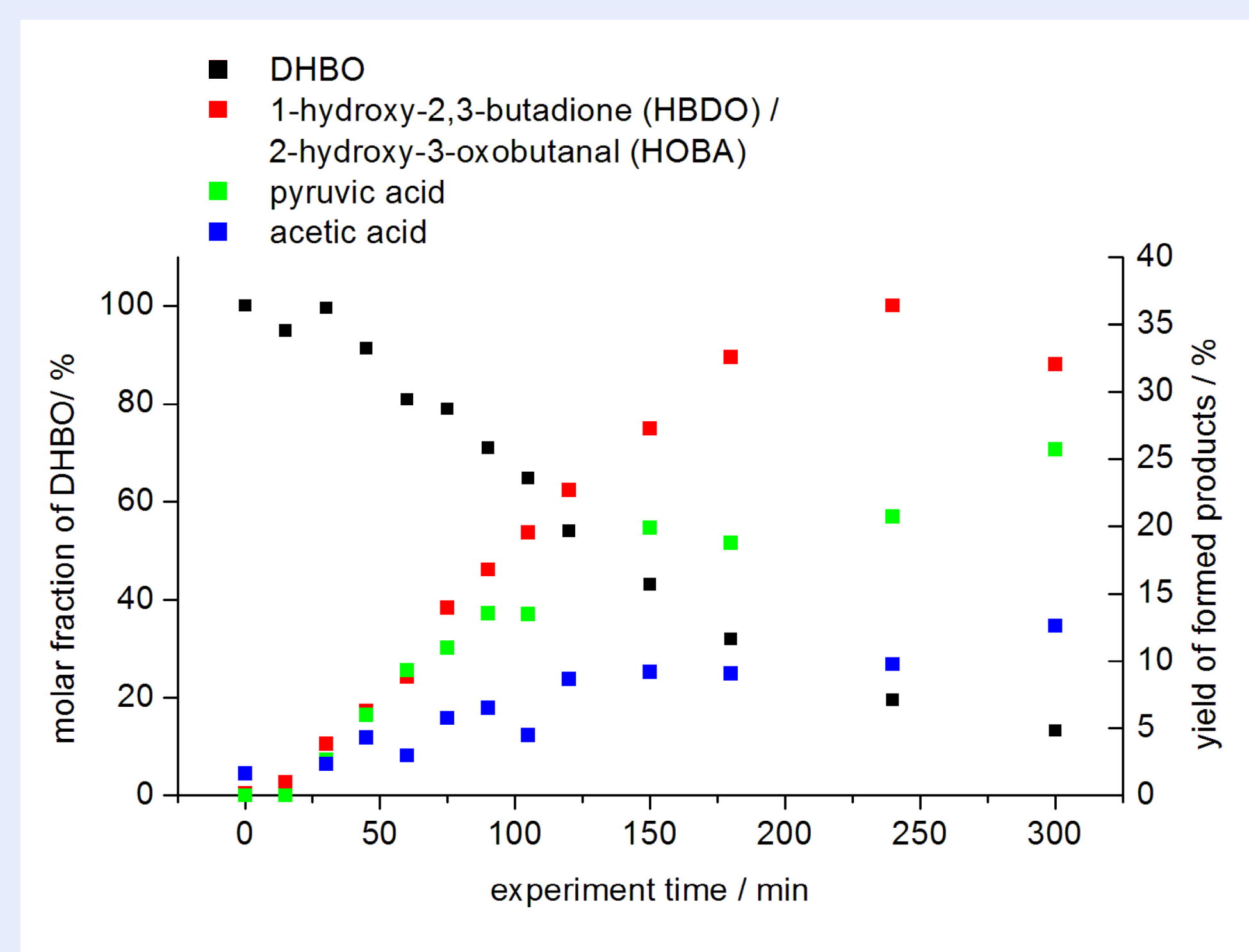
- Kinetic investigation of the radical-driven oxidation reactions of 3,4-dihydroxy-2-butanone (DHBO) and 2,3-dihydroxy-2-methylpropanal (DHMP) with OH, SO_4^- and NO_3 radicals in aqueous solution

Compound	OH	NO_3	SO_4^-
	$K_{2\text{nd}} (298 \text{ K}) / 10^7 (\text{L mol}^{-1} \text{ s}^{-1})$		
DHMP	(121 ± 20)	(0.8 ± 0.1)	(3.3 ± 0.2)
DHBO	(99 ± 21)	(0.3 ± 0.1)	(2.3 ± 0.1)

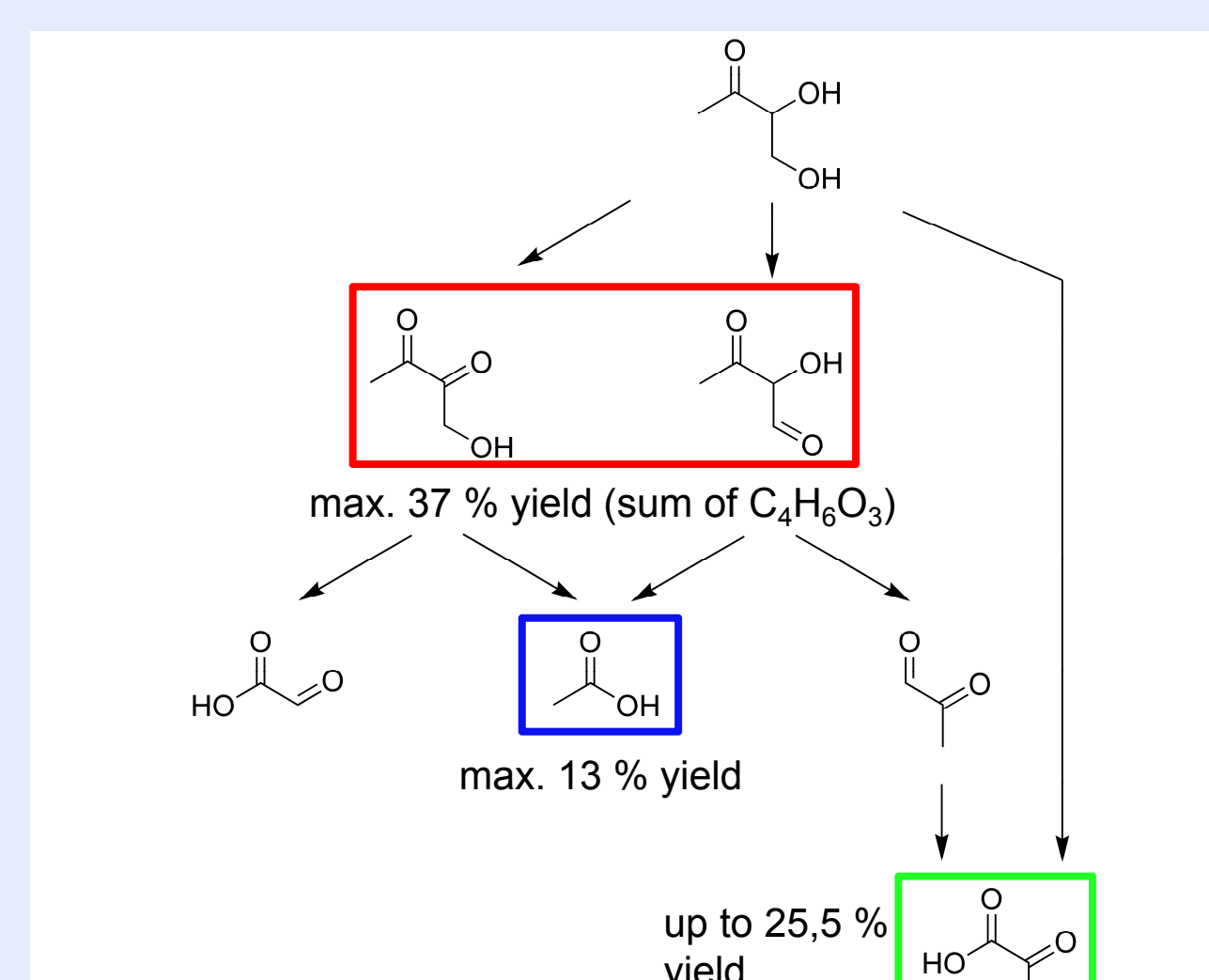


Compound	Radical	A / $\text{L mol}^{-1} \text{ s}^{-1}$	E_A / kJ mol^{-1}	ΔS^\ddagger / $\text{J K}^{-1} \text{ mol}^{-1}$
DHBO	OH	$(4.3 \pm 0.3) \times 10^9$	3.6 ± 4.4	-69.1 ± 5.4
	NO_3	$(4.9 \pm 0.1) \times 10^{11}$	30.1 ± 0.2	-29.5 ± 0.1
	SO_4^-	$(3.1 \pm 0.1) \times 10^9$	12.1 ± 1.6	-71.5 ± 2.1
DHMP	OH	$(5.5 \pm 0.1) \times 10^9$	3.7 ± 1.1	-66.8 ± 1.3
	NO_3	$(3.0 \pm 0.4) \times 10^{12}$	32.0 ± 9.1	-14.3 ± 1.8
	SO_4^-	$(2.4 \pm 0.2) \times 10^9$	10.5 ± 4.3	-73.8 ± 6.0

OH-driven oxidation of DHBO

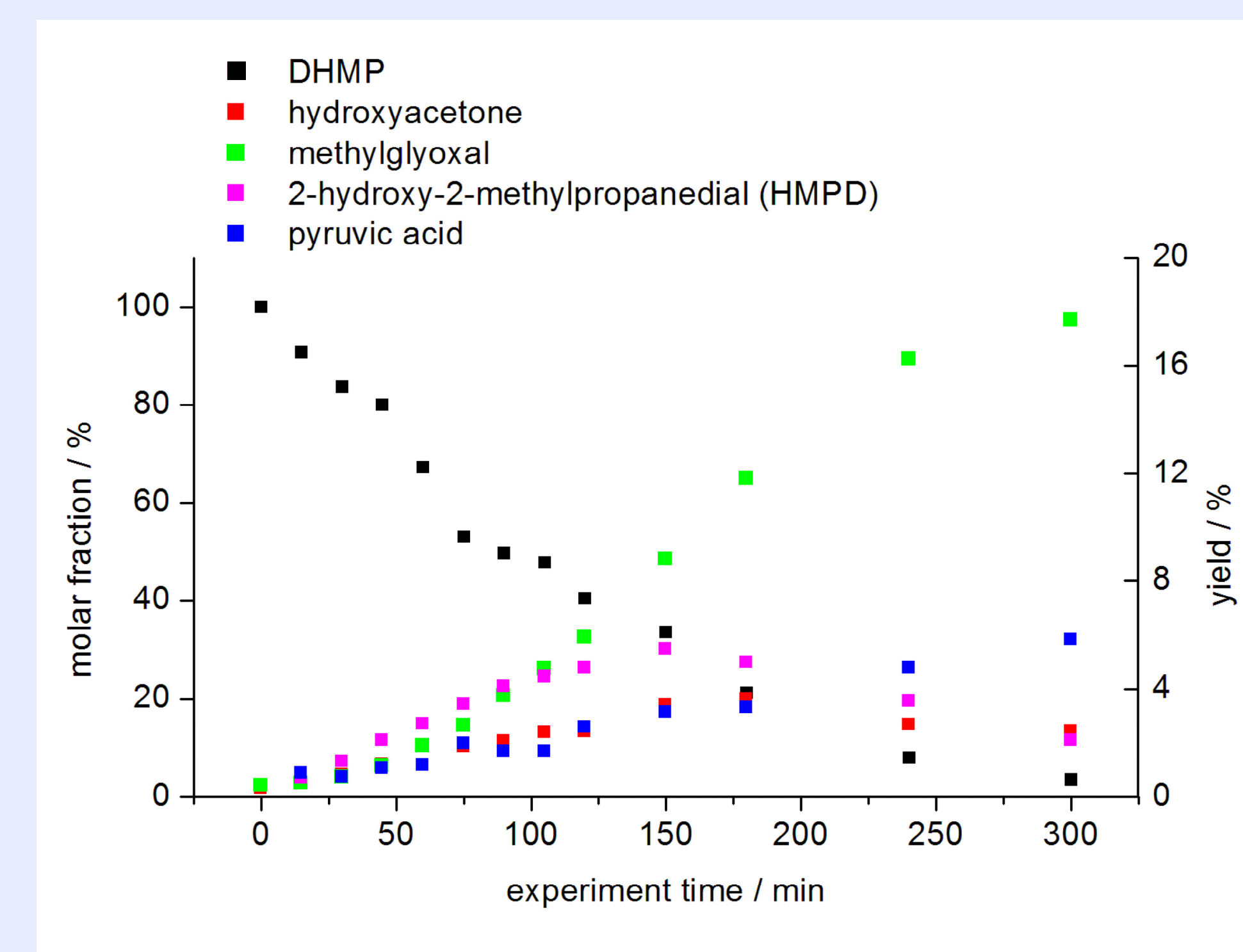


- Most common first generation oxidation products HBDO and HOBA, in general hydroxydicarbonyl compounds
- Quantification of the sum of hydroxydicarbonyl compounds via methylglyoxal as surrogate

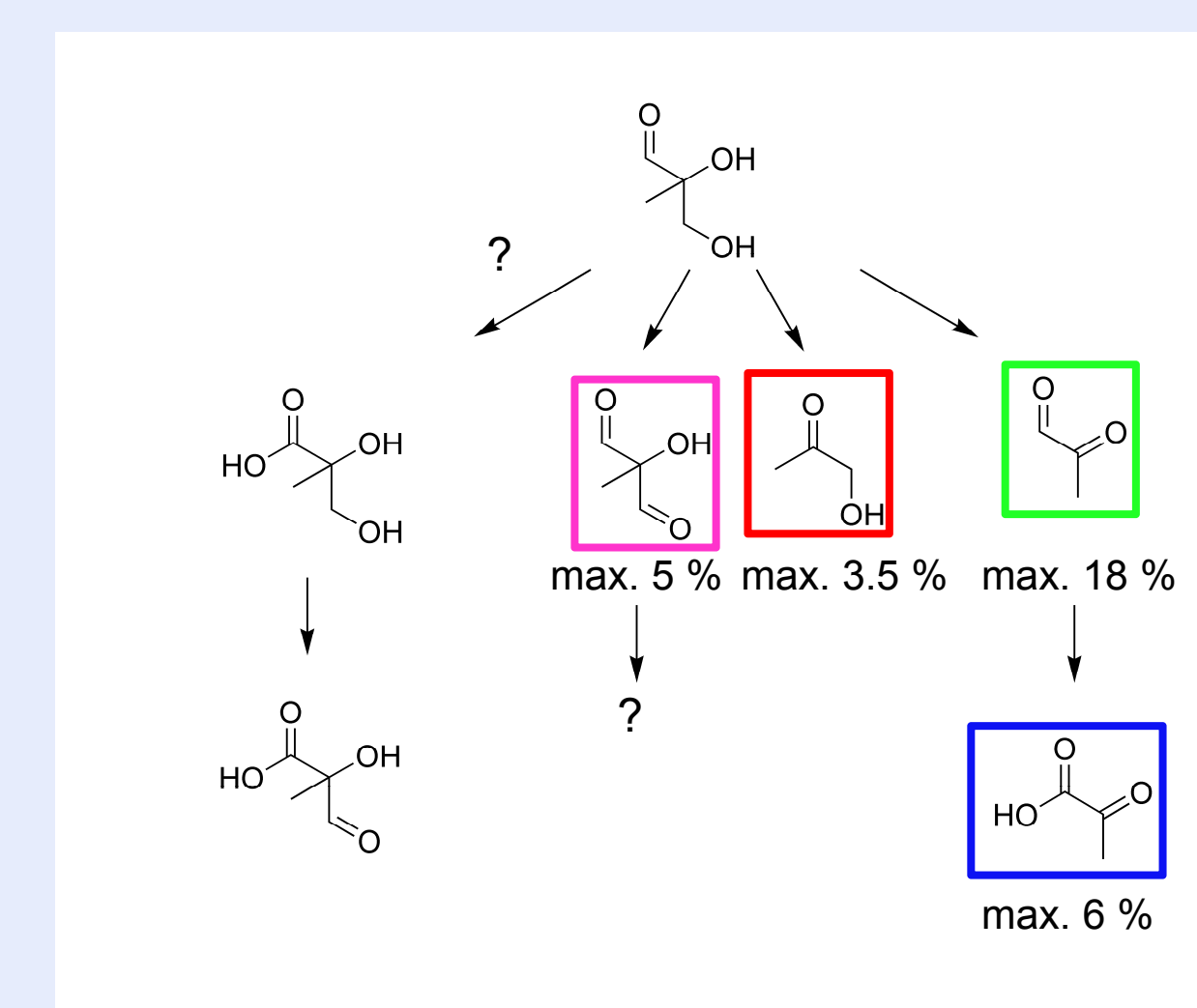


- Minor production with yields less than 10 % of glycolaldehyde, glyoxal, biacetyl, methylglyoxal, oxalic and glyoxylic acid
- Overall identified mass conversion of 70 %

OH-driven oxidation of DHMP



- Identification of methylglyoxal as most abundant oxidation product, with a yield of 18 %
- Quantification of the hydroxydicarbonyl compound HMPD as a minor product, due to its stability



- Missing identification and quantification of the supposed functionalized acid species
- Overall identified mass conversion of 30 %

Outlook

- Investigation of the impact of a changing ionic strength and a changing matrix composition
- Ongoing studies of the isoprene oxidation products in the aqueous phase to enhance the understanding of the mechanism, especially in terms of the quantification of the supposed dicarbonyl species and functionalized acid compounds
- Implementation of the obtained data in the Chemical Aqueous Phase Radical Mechanism (CAPRAM)

Acknowledgement

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References

- Sindelarova, K.; Granier, C.; Bouarar, I.; Guenther, A.; Tilmes, S.; Stavrou, T.; Müller, J. F.; Kuhn, U.; Stefani, P.; Knorr, W. *Atmos. Chem. Phys.* **2014**, *14*, 9317.
- Bates, K.; Nguyen, T.; Teng, A.; Crouse, J.; Kjaergaard, H.; Stoltz, B.; Seinfeld, J.; Wennberg, P. *J. Phys. Chem. A* **2016**, *120*, 106.
- White, J. U. *J. Opt. Soc. Am.* **1942**, *32*, 285.
- Rodigast, M.; Mutzel, A.; Iinuma, Y.; Haferkorn, S.; Herrmann, H. *Atmos. Meas. Tech.* **2015**, *8*, 2409.