

Aqueous-Phase Oxidation Kinetics of Terpene-Derived Compounds

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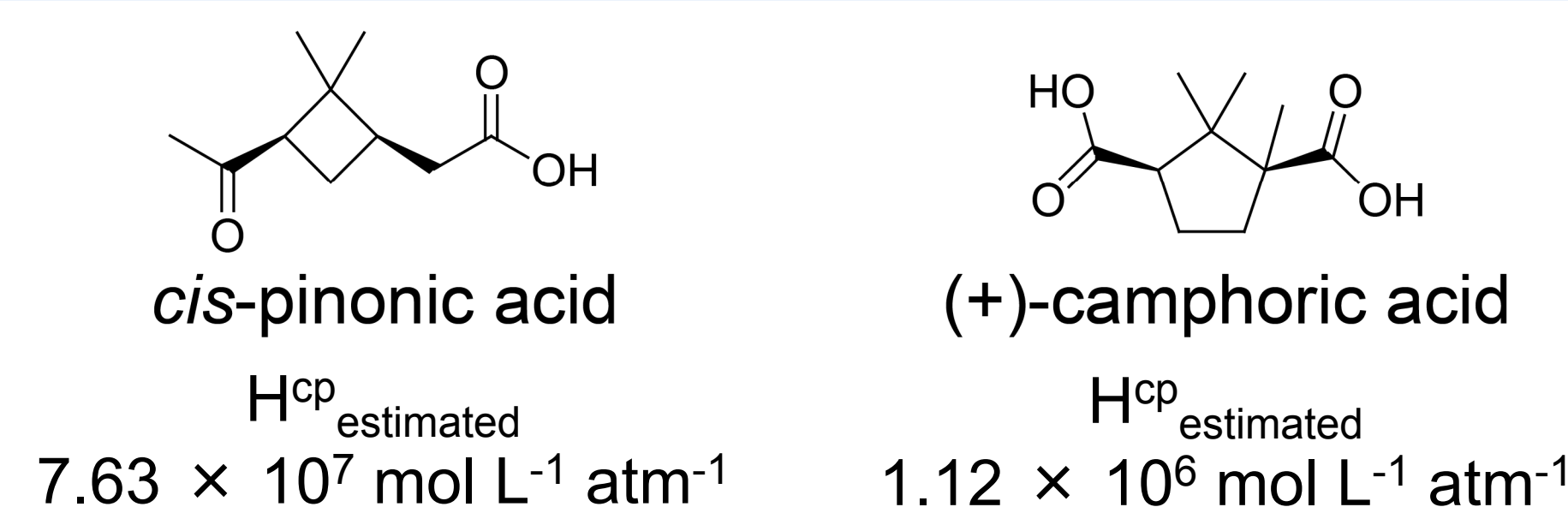
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Motivation

Within the past years, the tropospheric aqueous phase is increasingly getting into focus to be important for the formation of a significant fraction of secondary organic aerosol (SOA), addressed as aqueous secondary aerosol (aqSOA). A major fraction of SOA formed in the gas phase is originated from the oxidation of emitted biogenic volatile organic compounds (BVOCs), such as isoprene and terpenes in their entirety. The vast majority of aqueous-phase processes of terpene-derived compounds is still insufficiently studied.

Therefore, we investigated the oxidation reaction kinetics of *cis*-pinonic acid and (+)-camphoric acid towards hydroxyl (OH), nitrate (NO₃) and sulfate (SO₄⁻) radicals in aqueous solution.



Experimental: Laser Flash Photolysis – Long Path Absorption setup

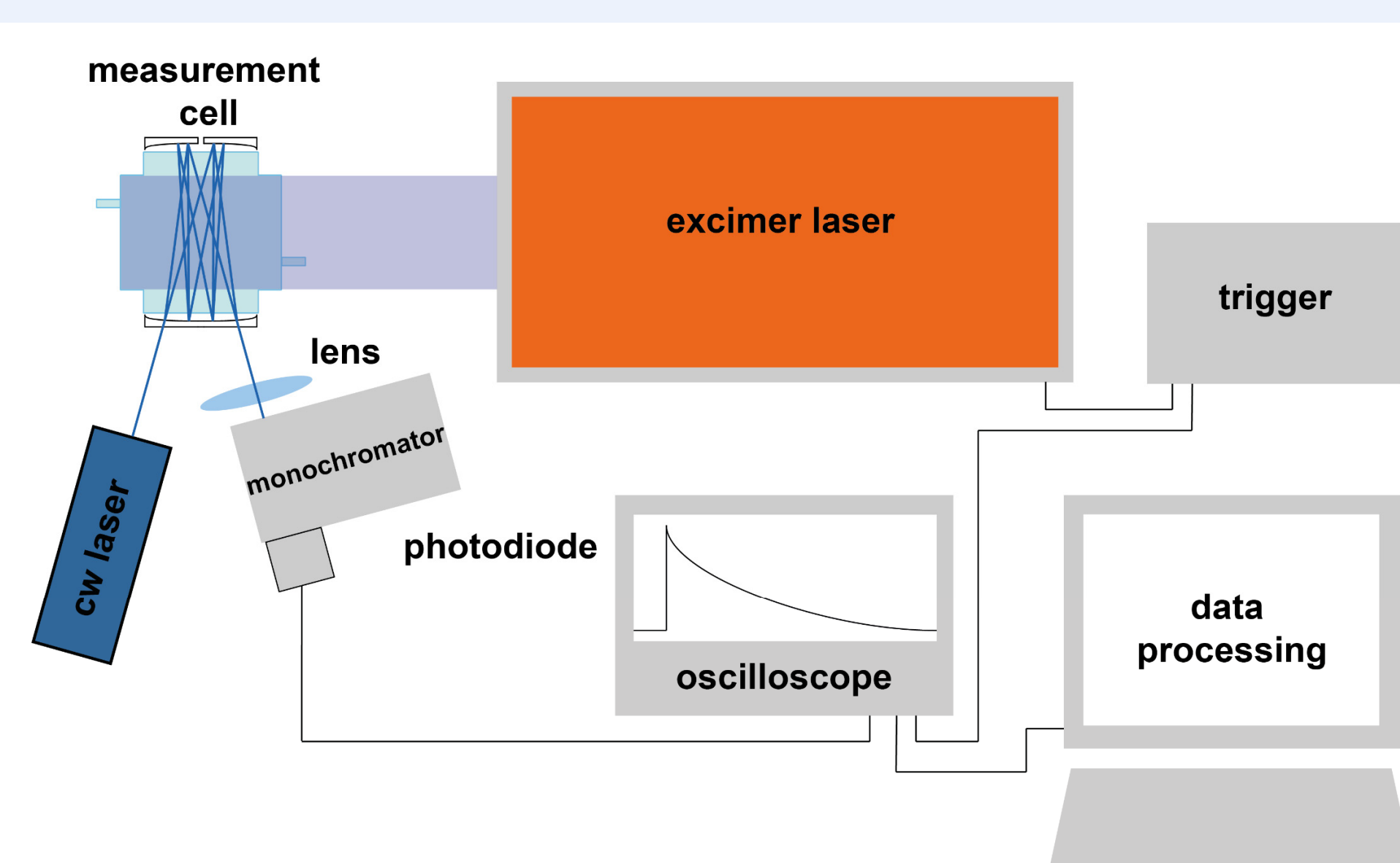


Figure 1: Scheme of the LFP-LLPA setup for kinetic investigations.¹

- Long path absorption by a White Mirror Cell²
- Organic reactant concentration up to $5 \times 10^{-4} \text{ M}$
- Direct observation of the decay of SO₄⁻ and NO₃
- In case of hydroxyl radicals observation of the competing reference system of SCN⁻:



Table 1: Experimental Conditions.

radical	$\lambda_{\text{Photo}} / \text{nm}$	$\lambda_{\text{Obs}} / \text{nm}$	measurement specifications	precursors
hydroxyl radical (OH)	248	473	competition kinetics	[H ₂ O ₂] = $2 \times 10^{-4} \text{ M}$ [SCN ⁻] = $2 \times 10^{-5} \text{ M}$
sulfate radical (SO ₄ ⁻)	248	473	direct measurement	[S ₂ O ₈ ²⁻] = $2.5 \times 10^{-4} \text{ M}$
nitrate radical (NO ₃)	351	635	direct measurement	[S ₂ O ₈ ²⁻] = 0.03 M / [NO ₃ ⁻] = 0.1 M

Results

- Kinetic investigation of the radical-driven oxidation reactions of *cis*-pinonic acid (CPA) and (+)-camphoric acid (+CA) with OH, SO₄⁻ and NO₃ radicals in aqueous solution
- Determination of second order rate constants in a temperature range from 278 K to 318 K

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

Compound	pH	k _{2nd} / 10 ⁷ L mol ⁻¹ s ⁻¹		
		OH	NO ₃	SO ₄ ⁻
<i>cis</i> -pinonic acid	1.0	(283 ± 12)	--	(2.6 ± 0.5)
	8.0	(266 ± 28)	--	(2.0 ± 0.1)
	8.6	--	(1.6 ± 0.1)	--
(+)camphoric acid	1.0	(211 ± 8)	--	(2.1 ± 0.1)
	5.3	--	(3.9 ± 0.4)	--
	8.0	(270 ± 7)	--	(1.5 ± 0.1)
	8.2	--	(5.9 ± 0.2)	--

- Second order rate constant of *cis*-pinonic acid with OH radicals ~ 21% lower than the recently published value of $(3.6 \pm 0.3) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$
- OH reaction rate constants superior to SO₄⁻ and NO₃
- General order of reactivity: OH > SO₄⁻ ≈ NO₃
- Strong temperature-dependence of nitrate kinetics compared to OH and SO₄⁻, leading to an increased activation energy of these reactions

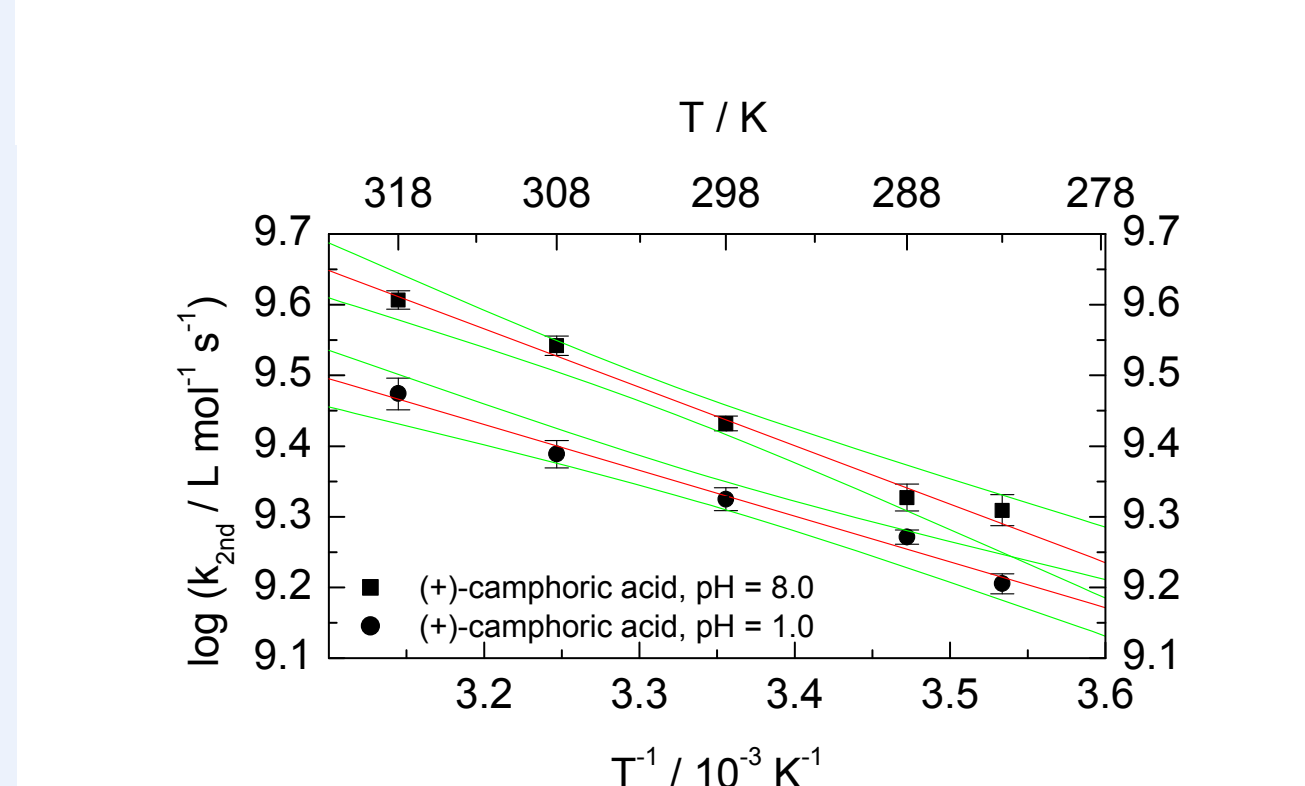
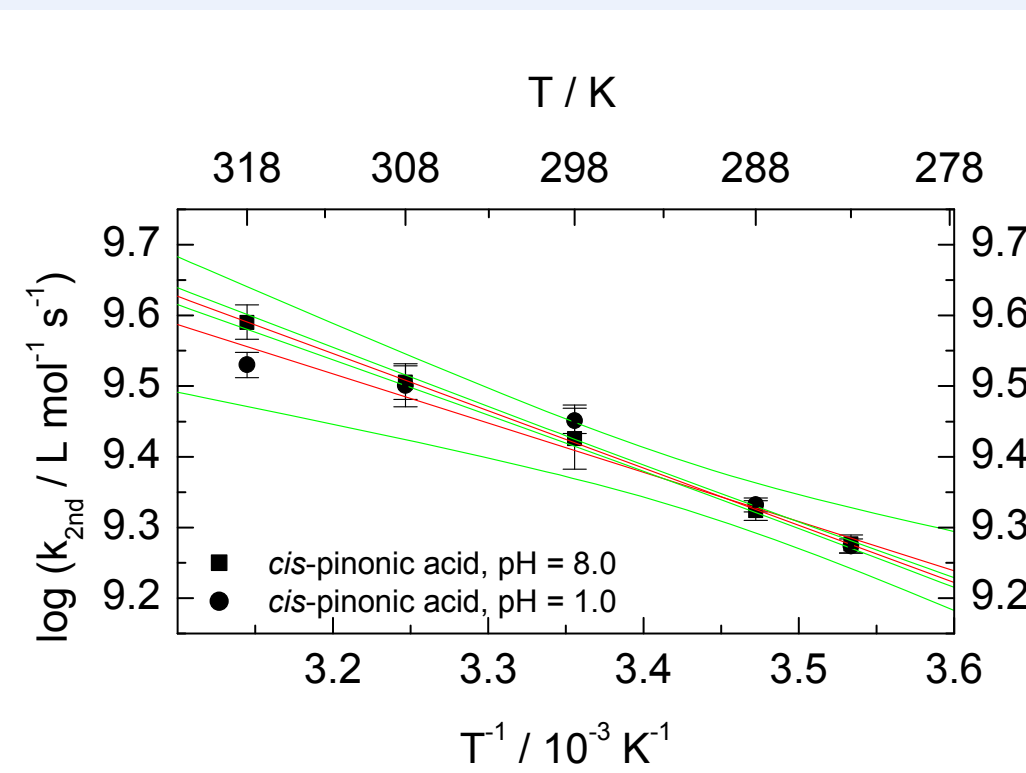


Figure 2: Temperature dependences of the reactions of CPA and +CA with OH radicals (linear regression in red and 95 % confidence interval in green).

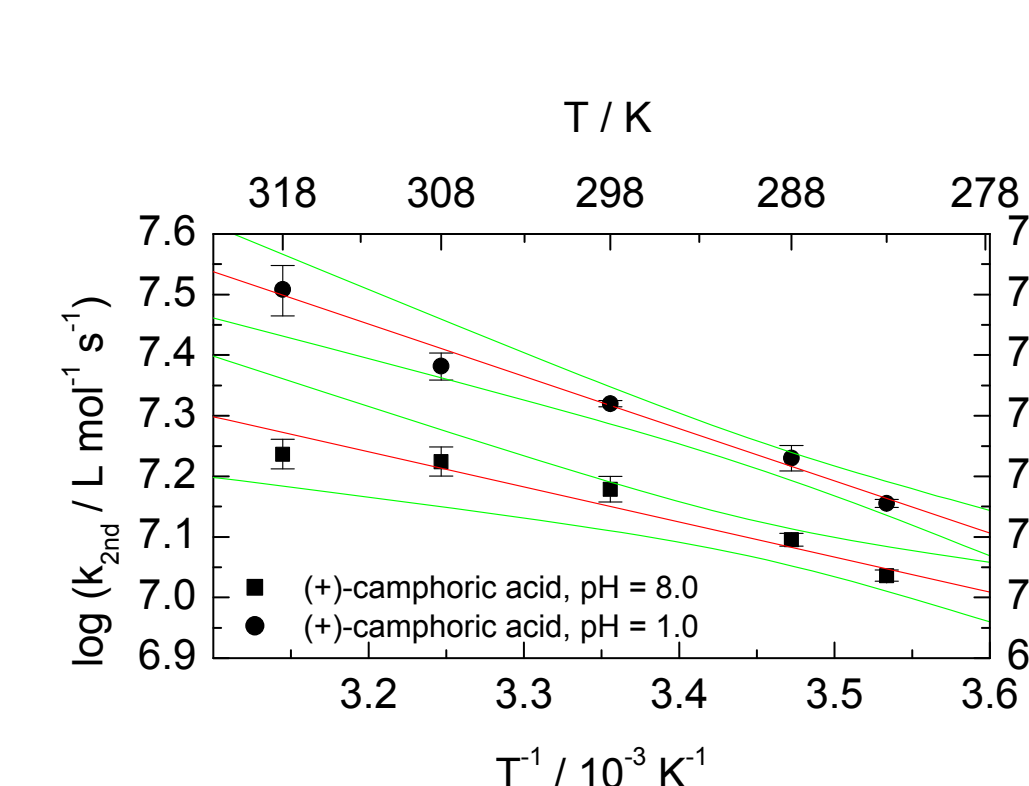
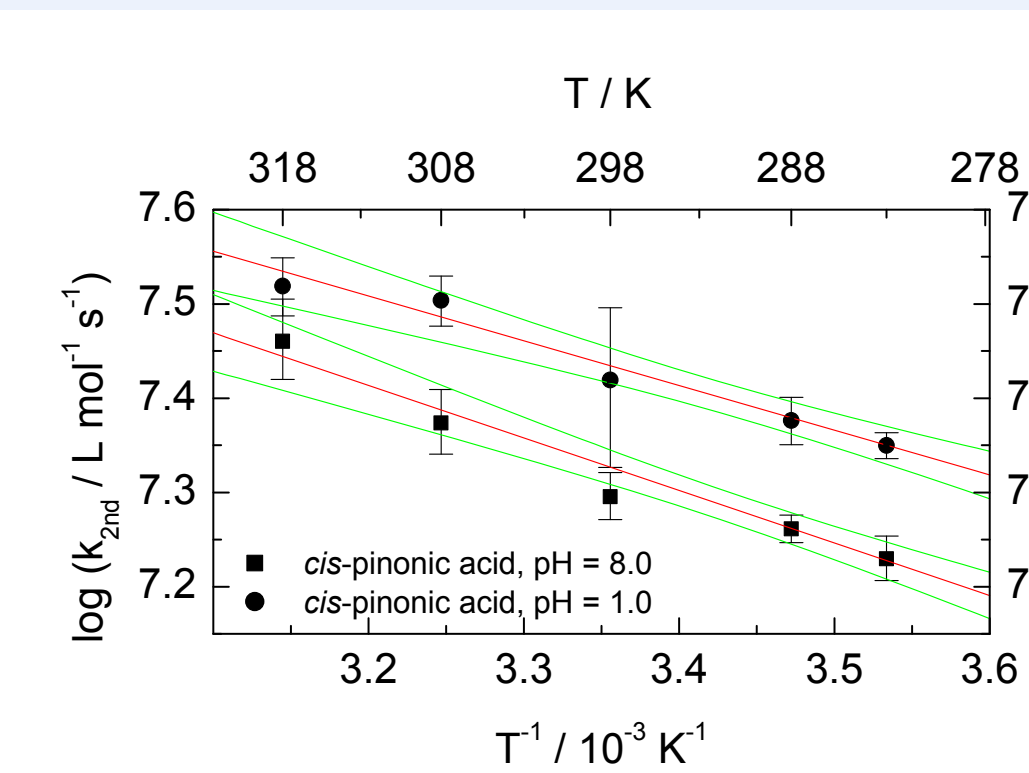


Figure 3: Temperature dependences of the reactions of CPA and +CA with SO₄⁻ radicals (linear regression in red and 95 % confidence interval in green).

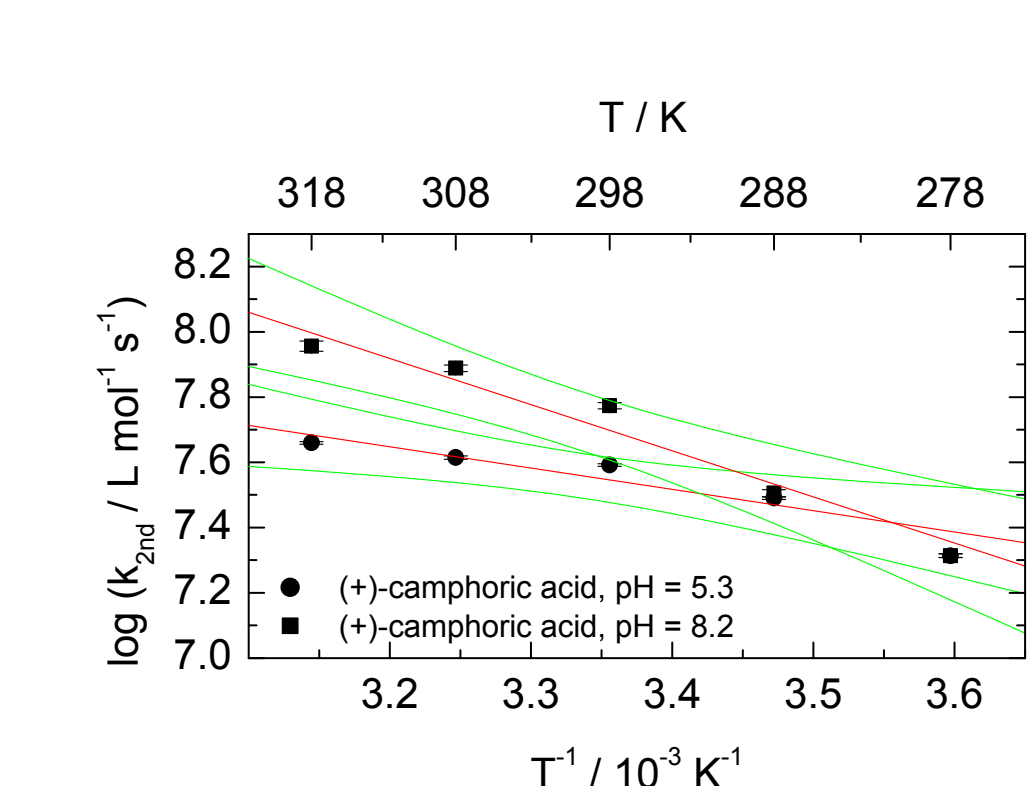
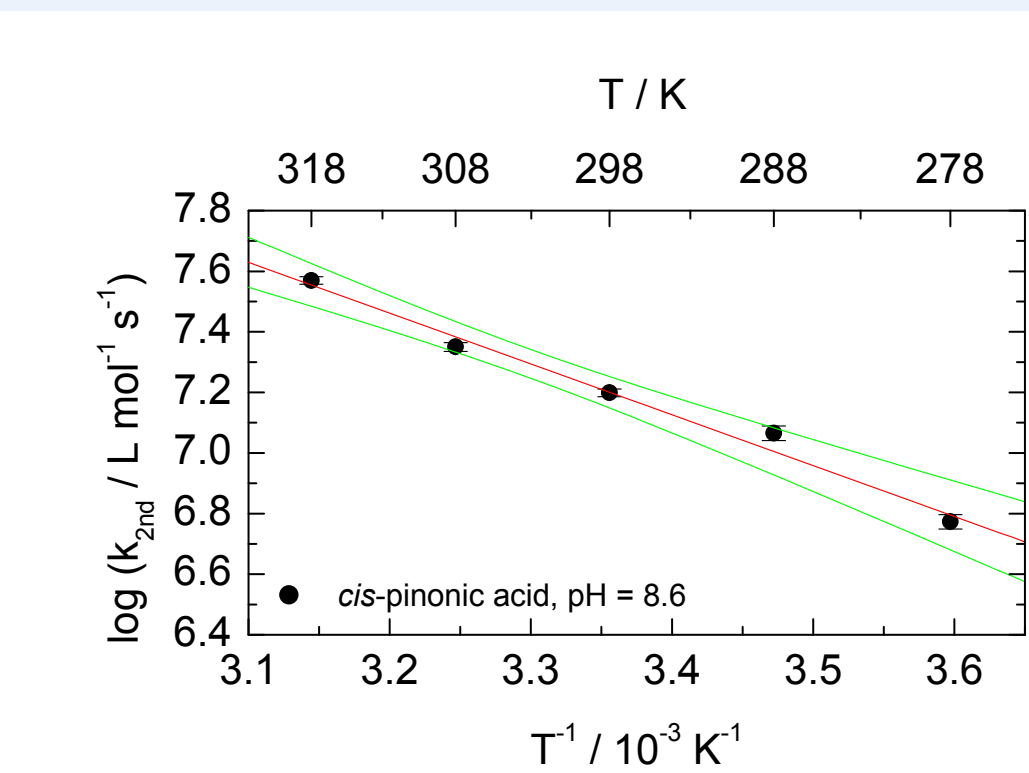


Figure 2: Temperature dependences of the reactions of CPA and +CA with NO₃ radicals (linear regression in red and 95 % confidence interval in green).

Table 3: Calculated activation parameters of the investigated reactions.

Compound	pH	Radical	A / L mol ⁻¹ s ⁻¹	E _A / kJ mol ⁻¹	ΔG [‡] / kJ mol ⁻¹	ΔH [‡] / kJ mol ⁻¹	ΔS [‡] / J K ⁻¹ mol ⁻¹
<i>cis</i> -pinonic acid	1.0	OH	$(5.6 \pm 0.2) \times 10^{11}$	13.3 ± 2.5	19.3 ± 4.3	10.9 ± 2.0	$-(28.3 \pm 1.1)$
		SO ₄ ⁻	$(1.1 \pm 0.1) \times 10^9$	9.1 ± 1.9	30.6 ± 7.6	6.6 ± 1.4	$-(80.4 \pm 3.1)$
	> 8	OH	$(1.3 \pm 0.1) \times 10^{12}$	15.4 ± 3.2	19.2 ± 4.9	13.0 ± 2.7	$-(21.1 \pm 1.0)$
(+)camphoric acid		SO ₄ ⁻	$(1.2 \pm 0.1) \times 10^9$	10.1 ± 3.6	31.2 ± 13.2	7.6 ± 2.7	$-(79.1 \pm 5.5)$
		NO ₃	$(6.8 \pm 0.2) \times 10^{12}$	32.1 ± 2.6	31.9 ± 3.7	29.6 ± 2.4	$-(7.6 \pm 0.3)$
	1.0	OH	$(3.2 \pm 0.1) \times 10^{11}$	12.4 ± 2.3	19.8 ± 4.4	9.9 ± 1.9	$-(33.0 \pm 1.2)$
		SO ₄ ⁻	$(2.1 \pm 0.1) \times 10^{10}$	17.1 ± 0.8	31.2 ± 2.0	14.6 ± 0.7	$-(55.7 \pm 0.8)$
	5.3	NO ₃	$(5.5 \pm 0.1) \times 10^9$	12.5 ± 0.7	29.9 ± 1.9	10.0 ± 0.5	$-(66.8 \pm 0.8)$
	> 8	OH	$(1.6 \pm 0.1) \times 10^{12}$	15.8 ± 2.7	19.1 ± 4.0	13.3 ± 2.3	$-(19.5 \pm 0.7)$
		SO ₄ ⁻	$(1.2 \pm 0.1) \times 10^9$	11.0 ± 4.5	32.2 ± 15.9	8.6 ± 3.5	$-(79.3 \pm 7.0)$
		NO ₃	$(4.8 \pm 0.6) \times 10^{12}$	28.4 ± 8.9	29.1 ± 12.6	25.9 ± 8.1	$-(10.5 \pm 1.3)$

Conclusion and Outlook

- First insights into the temperature-dependent aqueous-phase reaction kinetics of *cis*-pinonic acid and (+)-camphoric acid towards atmospheric oxidizing agents
- Pending lack of knowledge on the aqueous phase kinetics and mechanisms of related compounds
- Product studies of the oxidation products of the kinetically investigated compounds in the aqueous phase required to enhance the understanding of their aqueous-phase oxidation mechanism
- Implementation of the obtained data in the Chemical Aqueous Phase Radical Mechanism

References

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- 2) White, J. U. (1942), Long Optical Paths of Large Aperture, *J. Opt. Soc. Am.*, 32, 285-288.
- 3) Witkowski, B. and Gierczak, T. (2017), *cis*-Pinonic Acid Oxidation by Hydroxyl Radicals in the Aqueous Phase under Acidic and Basic Conditions: Kinetics and Mechanism, *Environ. Sci. Technol.*, 51, 9765-9773.