

# Temperature dependent kinetic measurements of isoprene oxidation products

exposed to OH, NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup>



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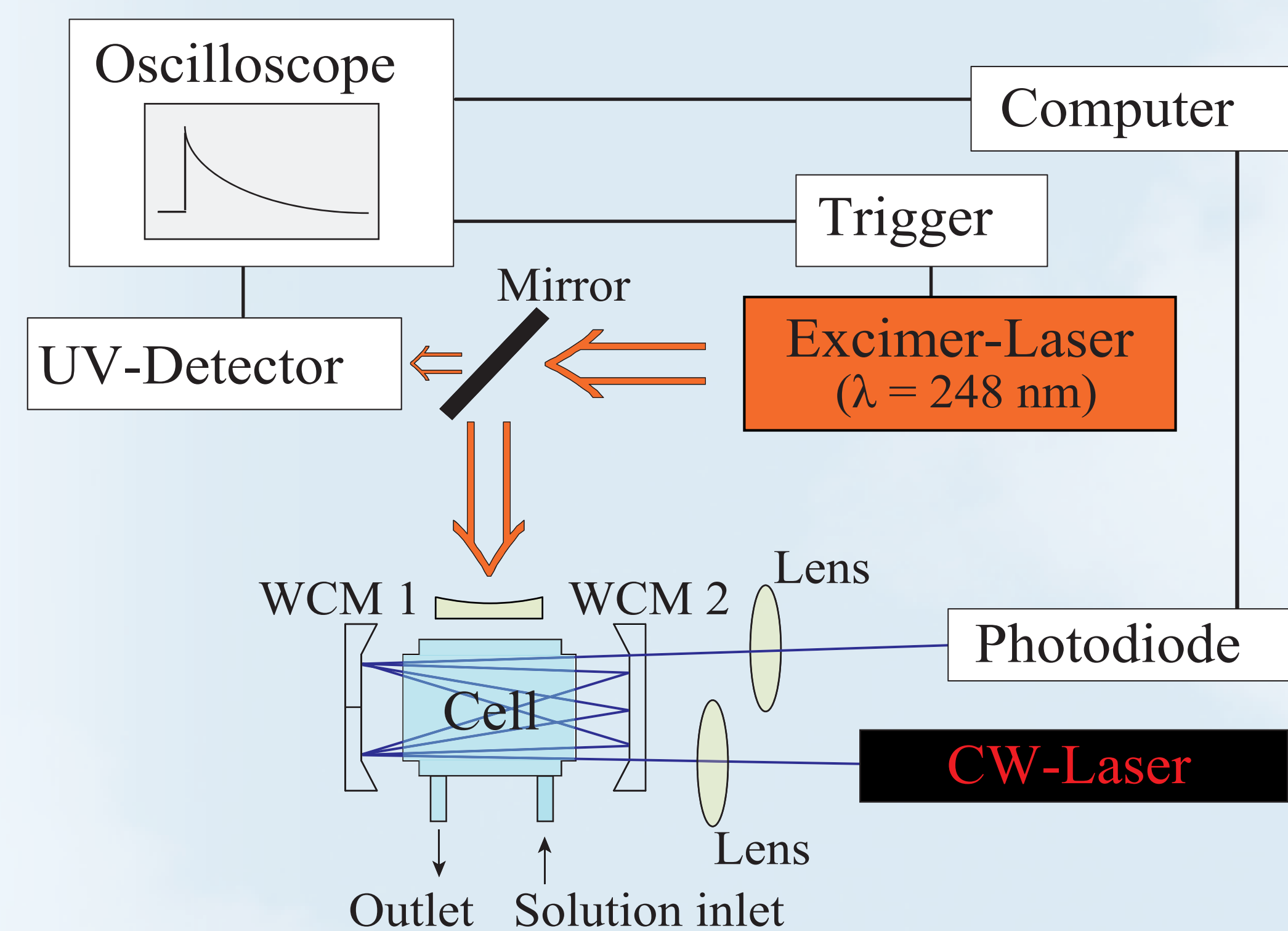
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## Motivation

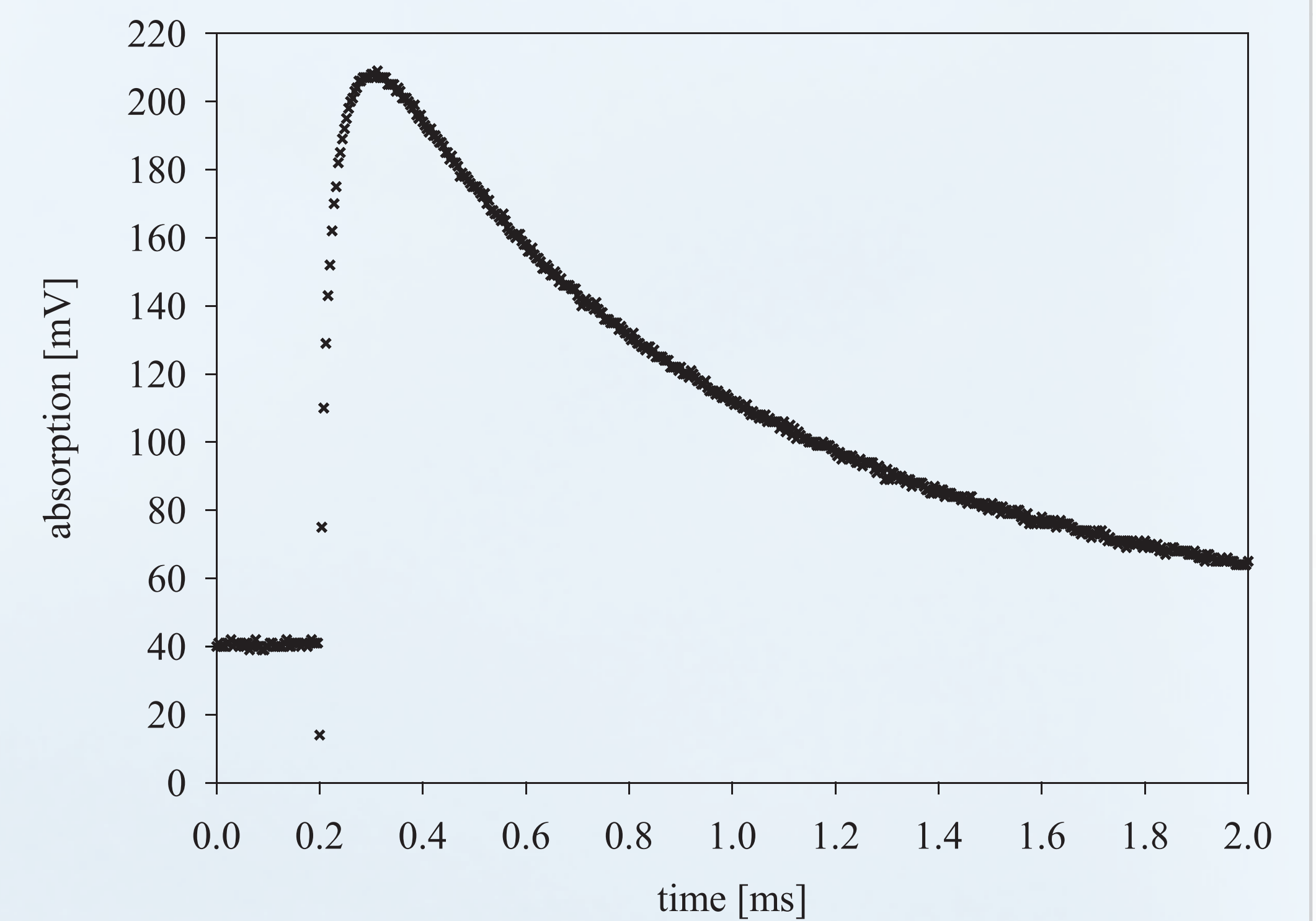
The troposphere contains a complex mixture of numerous gases, liquid water and diverse solid particles which undergo intricate processes. Volatile organic compound (VOC) emissions from anthropogenic and biogenic sources are very important for the tropospheric chemistry and other processes such as secondary organic particle mass formation. Emissions of biogenic volatile organic compounds (BVOCs) exceed those coming from human activity by a factor of 10<sup>a</sup>. Isoprene (2-methyl-1,3-butadiene, C<sub>5</sub>H<sub>8</sub>) emissions represent approximately 40 % of the emitted BVOCs, leading to an estimated source strength of 500-750 Tg yr<sup>-1 b</sup>. As isoprene has a small Henry coefficient, its oxidation occurs solely in the gas phase. The formed first oxidation products methacrolein (MACR), methyl vinyl ketone (MVK), methacrylic acid (MAA) and acrylic acid (ACA) are therefore firstly located in that phase. Even if the Henry coefficients of the main isoprene oxidation products MACR and MVK are already higher than those of isoprene partitioning of these compounds into the aqueous phase of rain, fog and cloud droplets and particles was neglected. Correspondingly, aqueous phase oxidation processes of MACR and MVK were sparsely investigated in the past. A recent study<sup>c</sup>, however, reports much higher aqueous phase concentrations of MACR and MVK than expected from their Henry coefficients. Aqueous phase models for the evaluation of the importance of liquid phase reactions of early isoprene oxidation products for the organic particle mass production therefore need extensive kinetic data.

## Experimental



**Figure 1:** Scheme of the laser photolysis setup used for the kinetic studies in aqueous solution.

- Kinetic studies were performed using a laser photolysis laser long path absorption (LP-LLPA) technique (Figure 1).
- The solution contains precursor substances for the radicals and the investigated organic compound.
- Used precursor substances are [H<sub>2</sub>O<sub>2</sub>] = 1 · 10<sup>-4</sup> mol L<sup>-1</sup> for the hydroxyl radical OH, [NaNO<sub>3</sub>] = 0.1 mol L<sup>-1</sup> and [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 0.03 mol L<sup>-1</sup> for the nitrate radical NO<sub>3</sub> and [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] = 5 · 10<sup>-4</sup> mol L<sup>-1</sup> for the sulfate radical SO<sub>4</sub><sup>-</sup>.
- Radicals are generated by laser flash photolysis of the precursor compounds by the Excimer-Laser at λ = 248 nm.
- Reactions between the formed radicals and the organic compound change the absorption characteristics of the solution.
- Absorption-time-profiles (Figure 2) at different reactant concentrations are detected by a Continuous-Wave-Laser and a photodiode using a constellation of two White mirrors and are finally stored by an oscilloscope for further analysis.



**Figure 2:** Example for an absorption-time-profile for the reaction of NO<sub>3</sub> with acrylic acid, pH = 1, T = 298 K, [ACA] = 4 · 10<sup>-5</sup> mol L<sup>-1</sup>.

## Kinetic studies

The reactivity of methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid exposed to OH, NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> in aqueous solution was measured by laser flash photolysis. All kinetic studies were conducted as a function of temperature. The obtained data and existing literature values from the gas phase and the aqueous phase are summarized in Table 1 and 2 and Figure 3 and 4, respectively.

**Table 1:** Summary of rate constants at T = 298 K measured in this work (bold) and values from literature. The listed gas phase values [h] represent averaged data from the NIST database.

Compound	pH	OH			NO <sub>3</sub>			SO <sub>4</sub> <sup>-</sup>		
		k <sub>2nd</sub> (L mol <sup>-1</sup> s <sup>-1</sup> )			k <sub>2nd</sub> (L mol <sup>-1</sup> s <sup>-1</sup> )			k <sub>2nd</sub> (L mol <sup>-1</sup> s <sup>-1</sup> )		
methacrolein	~ 6	(1.0 ± 0.1) · 10 <sup>10</sup>	*	(3.0 ± 0.6) · 10 <sup>7</sup>		(9.9 ± 4.9) · 10 <sup>7</sup>				
		8.0 · 10 <sup>9</sup>	[d]	2.7 · 10 <sup>9</sup> (pH=3)	[f]	1.2 · 10 <sup>9</sup>	[d]			
		1.4 · 10 <sup>10</sup>	[g]	3.1 · 10 <sup>6</sup> (gas)	[h]					
		1.9 · 10 <sup>10</sup> (gas)	[h]							
methyl vinyl ketone	~ 6	(7.4 ± 0.7) · 10 <sup>9</sup>	*	(1.9 ± 0.3) · 10 <sup>7</sup>		(1.0 ± 0.2) · 10 <sup>8</sup>				
		1.1 · 10 <sup>10</sup> (gas)	[h]	2.2 · 10 <sup>5</sup> (gas)	[h]					
methacrylic acid	1	(1.2 ± 0.1) · 10 <sup>10</sup>	*	(7.7 ± 1.4) · 10 <sup>7</sup>		(2.5 ± 1.2) · 10 <sup>8</sup>				
	2.9					1.1 · 10 <sup>9</sup>	[e]			
	8	(1.2 ± 0.1) · 10 <sup>10</sup>	*	(2.1 ± 1.2) · 10 <sup>8</sup>		(3.5 ± 1.1) · 10 <sup>8</sup>				
acrylic acid	~ 7	1.6 · 10 <sup>10</sup>	[e]			7 · 10 <sup>8</sup>	[e]			
	1	(5.4 ± 0.8) · 10 <sup>9</sup>		(2.2 ± 0.1) · 10 <sup>7</sup>		(9.5 ± 0.8) · 10 <sup>7</sup>				
	8	(6.5 ± 1.0) · 10 <sup>9</sup>		(1.1 ± 0.5) · 10 <sup>8</sup>		(9.9 ± 2.0) · 10 <sup>7</sup>				
	7-7.2		5.7 · 10 <sup>9</sup>	[e]						
	6.5					1.1 · 10 <sup>8</sup>	[e]			

\* Measurements conducted by E. Szeremeta at the IFT within a promoted ACCENT project.

- OH radicals react fastest with the studied unsaturated reactands. The investigated reactions of OH radicals proceed almost diffusion controlled.
- The measured rate constants of OH with MACR, MVK, MAA and ACA in water show a good agreement with literature data and are similar to those in the gas phase.
- It is assumed that addition to a C=C double bond is the dominant reaction mechanism for all radicals.
- Order of reactivity: OH >> SO<sub>4</sub><sup>-</sup> > NO<sub>3</sub>, with SO<sub>4</sub><sup>-</sup> ≈ 3.5 · NO<sub>3</sub>, OH ≈ 200 · NO<sub>3</sub> and OH ≈ 60 · SO<sub>4</sub><sup>-</sup>.

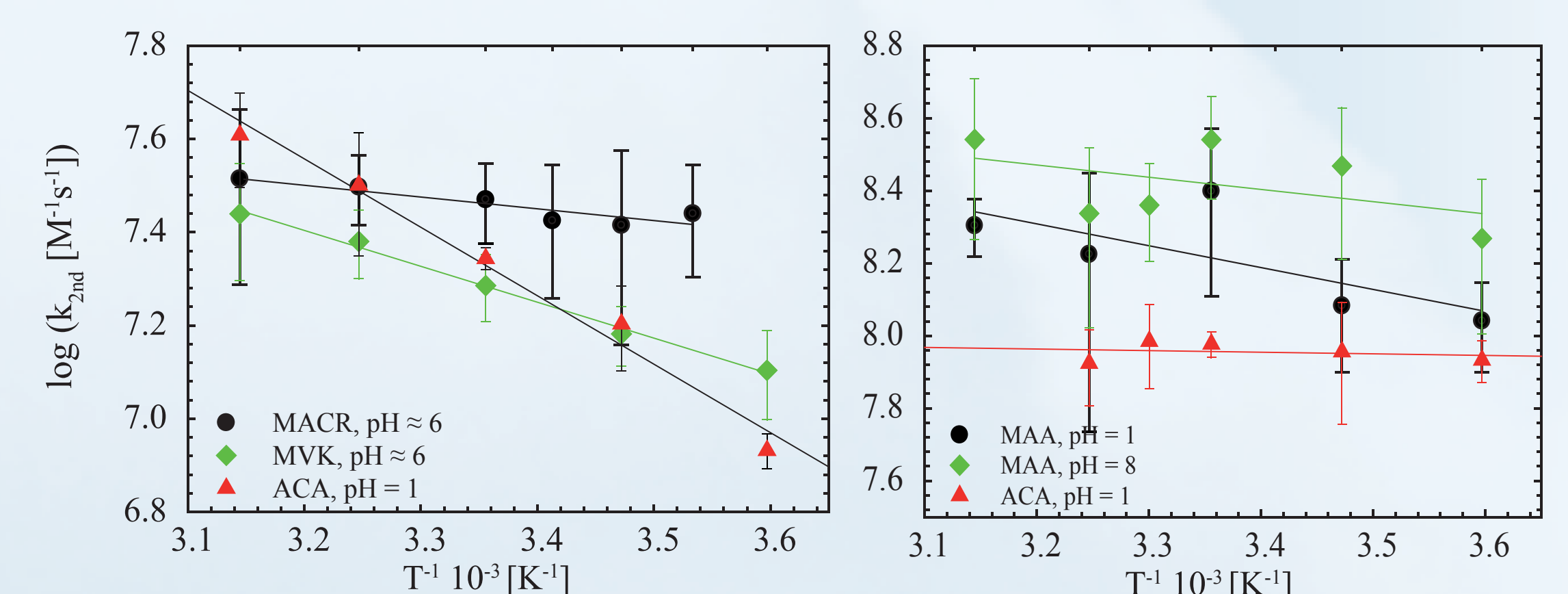
**Table 2:** Summary of calculated activation parameters from the measured temperature dependencies.

Reactant	A [L mol <sup>-1</sup> s <sup>-1</sup> ]	E <sub>a</sub> [kJ mol <sup>-1</sup> ]	ΔG <sup>‡</sup> [kJ mol <sup>-1</sup> ]	ΔH <sup>‡</sup> [kJ mol <sup>-1</sup> ]	ΔS <sup>‡</sup> [J K <sup>-1</sup> mol <sup>-1</sup> ]	
methacrolein	OH	(6.2 ± 0.6) · 10 <sup>11</sup>	(10 ± 6)	(16 ± 11)	(8 ± 5)	-(27 ± 2)
	NO <sub>3</sub>	(7.2 ± 1.0) · 10 <sup>7</sup>	(2 ± 6)	(30 ± 93)	-(0.3 ± 1.0)	-(103 ± 15)
	SO <sub>4</sub> <sup>-</sup>	-	-	-	-	-
methyl vinyl ketone	OH	(2.5 ± 0.2) · 10 <sup>11</sup>	(8 ± 6)	(16 ± 13)	(6 ± 4)	-(35 ± 3)
	NO <sub>3</sub>	(6.9 ± 0.3) · 10 <sup>9</sup>	(15 ± 2)	(31 ± 7)	(12 ± 2)	-(65 ± 3)
	SO <sub>4</sub> <sup>-</sup>	-	-	-	-	-
methacrylic acid pH = 1	OH	(1.2 ± 0.1) · 10 <sup>12</sup>	(11 ± 4)	(15 ± 6)	(9 ± 3)	-(21 ± 1)
	NO <sub>3</sub>	-	-	-	-	-
	SO <sub>4</sub> <sup>-</sup>	(1.2 ± 0.4) · 10 <sup>10</sup>	(11 ± 19)	(26 ± 56)	(8 ± 15)	-(60 ± 20)
methacrylic acid pH ≈ 8	OH	(2.1 ± 0.1) · 10 <sup>12</sup>	(12 ± 5)	(15 ± 7)	(10 ± 4)	-(17 ± 1)
	NO <sub>3</sub>	-	-	-	-	-
	SO <sub>4</sub> <sup>-</sup>	(3.5 ± 1.1) · 10 <sup>9</sup>	(6 ± 17)	(25 ± 72)	(4 ± 10)	-(70 ± 21)
acrylic acid pH = 1	OH	(1.1 ± 0.01) · 10 <sup>11</sup>	(7 ± 1)	(17 ± 2)	(5 ± 1)	-(42 ± 1)
	NO <sub>3</sub>	(1.6 ± 0.2) · 10 <sup>12</sup>	(28 ± 7)	(31 ± 11)	(25 ± 7)	-(19 ± 2)
	SO <sub>4</sub> <sup>-</sup>	(2.0 ± 0.2) · 10 <sup>8</sup>	(2 ± 4)	(28 ± 61)	-(1 ± 1)	-(94 ± 8)
acrylic acid pH ≈ 8	OH	(2.4 ± 0.06) · 10 <sup>10</sup>	(3 ± 1)	(17 ± 8)	(0.8 ± 0.3)	-(55 ± 1)
	NO <sub>3</sub>	-	-	-	-	-
	SO <sub>4</sub> <sup>-</sup>	-	-	-	-	-

- Partially strong deviations between literature data and measured results in this study for NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> radicals in Table 1.
- NO<sub>3</sub> reacts significantly faster in water than in the gas phase.
- The individual reactants show particularly for NO<sub>3</sub> distinct differences in the reactivity.
- Not all measured temperature dependencies yield linear Arrhenius plots. The effects (Table 2) are furthermore quite small in most of the cases.

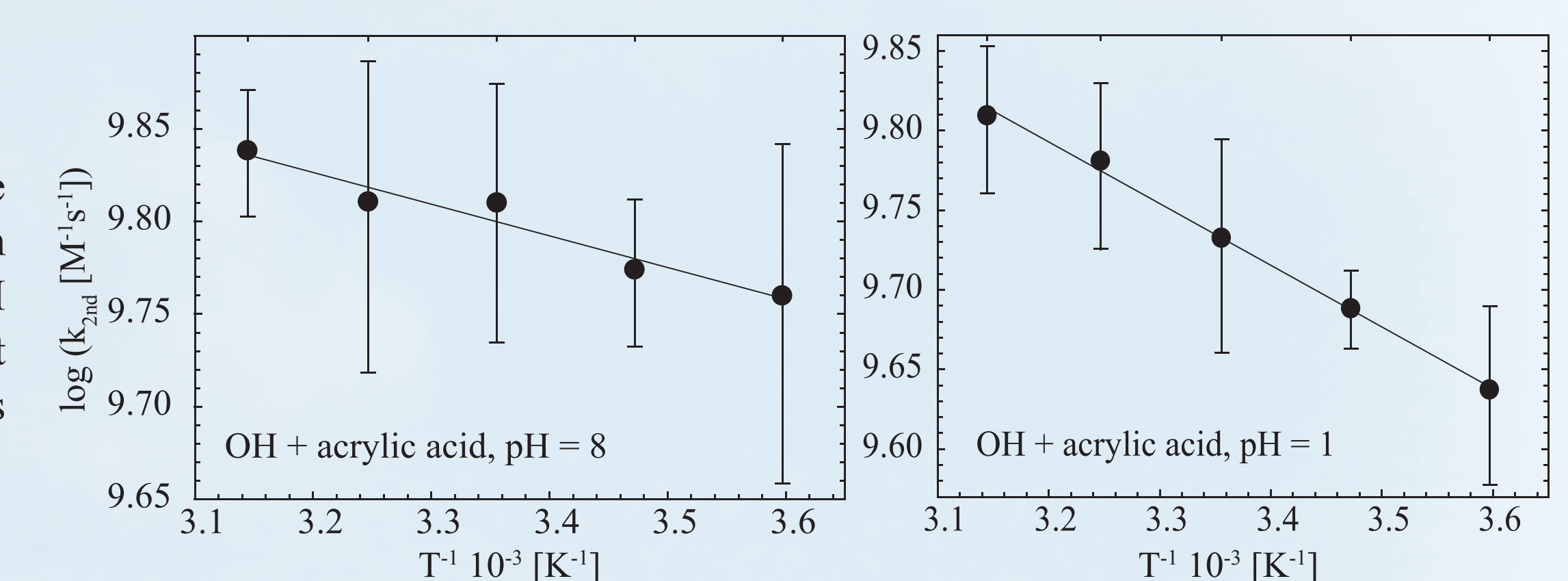
**Figure 3:**

Measured temperature dependencies for the reaction of NO<sub>3</sub> (left) and SO<sub>4</sub><sup>-</sup> radicals (right) in aqueous solution.



**Figure 4:**

Measured temperature dependencies for the reaction of acrylic acid with OH radicals for two different pH-values in aqueous solution.



## Summary and Outlook

The reactivity of four isoprene oxidation products exposed to OH, NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> radicals as a function of temperature in aqueous solution was examined. The kinetic measurements showed a significantly faster reaction of OH with all four reactants compared with the other two radicals. The measured rate constants in aqueous solution are thereby partially higher than those in the gas phase.

The implementation of the obtained kinetic results in already existing multiphase mechanisms (e.g. CAPRAM 3.0) may help to clarify the role of processes occurring within the aqueous phase during the oxidation of isoprene. Considering that later isoprene oxidation products are important constituents of atmospheric particles, this can be a useful tool to improve the understanding of the formation of secondary organic aerosols which have a considerable impact on e.g. cloud droplet generation.

## References

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