# Kinetic Studies of Imidazoles in Tropospheric Aqueous-Phase Chemistry: Photochemistry of Imidazole-2-carboxaldehyde and Oxidation Reactions with Hydroxyl Radicals

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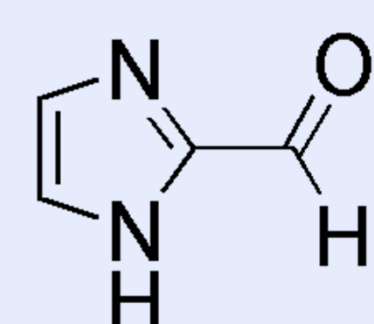
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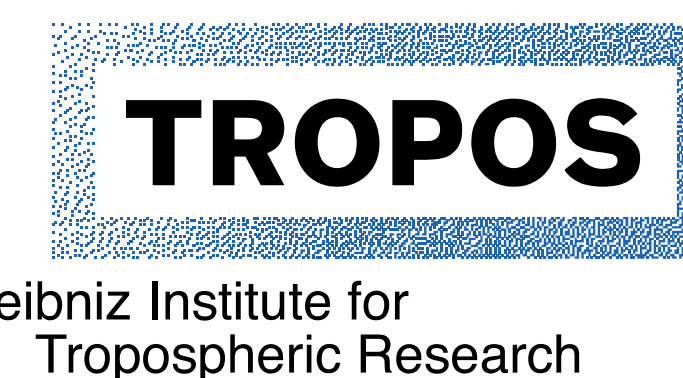
Introduction

Imidazoles

- Aromatic heterocycles with non-adjacent nitrogen atoms
- Light absorbing properties in the UV-region (200 – 380 nm)

Imidazole-2-carboxaldehyde (IC)

- Formation of imidazoles via reaction of α,β-dicarbonyls with nitrogen containing compounds
- Quantification of imidazoles in ambient aerosol particles
  - Concentration range: $0.2 – 14$ ng/m^3
  - 4(5)-Methylimidazole, 1-Ethylimidazole, 2-Ethylimidazole, 1-Butylimidazole, **Imidazole-2-carboxaldehyde**
- Imidazole-2-carboxaldehyde as potential photosensitizer
  - Initiation of secondary organic aerosol (SOA) growth
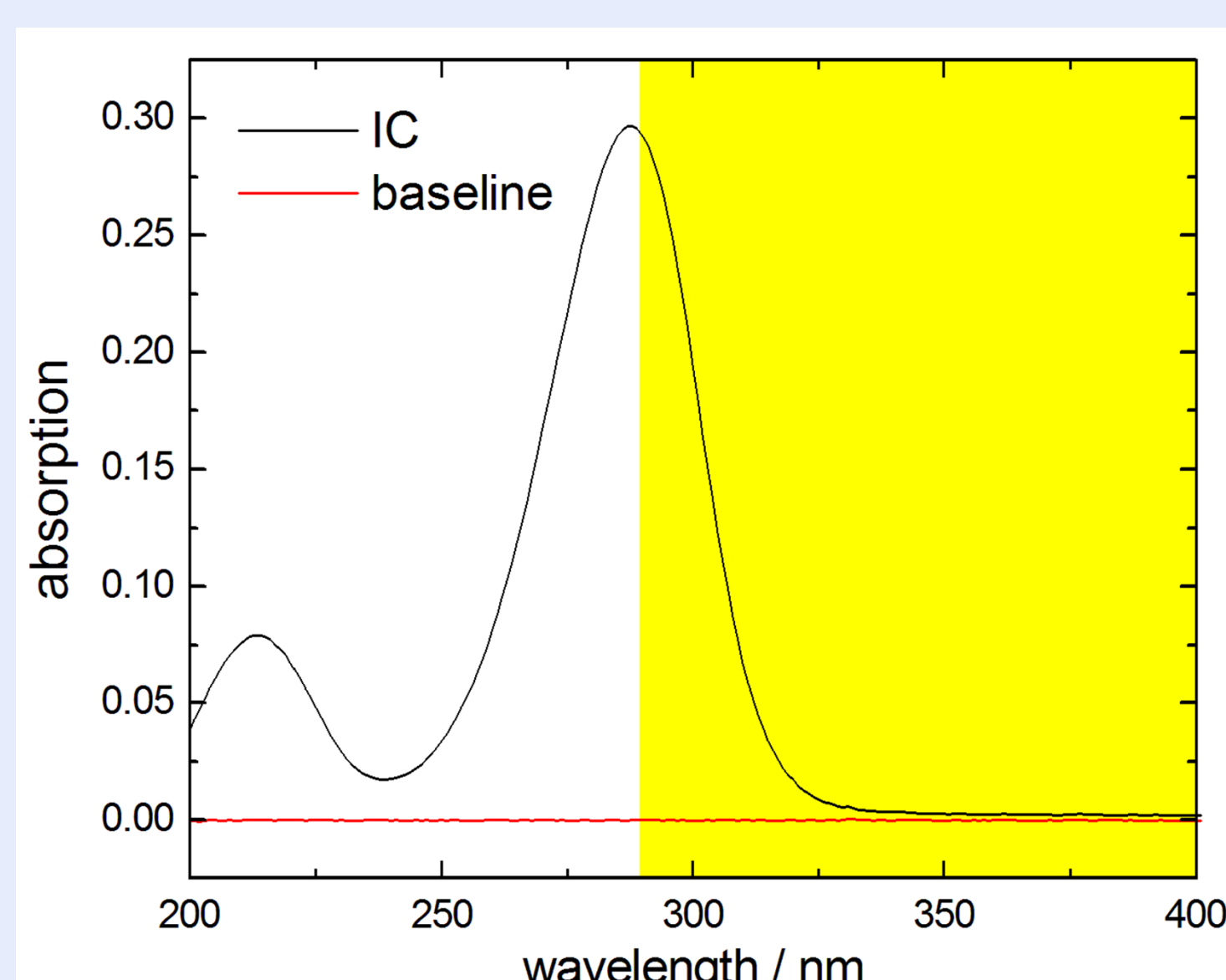 - Reaction with halide anions

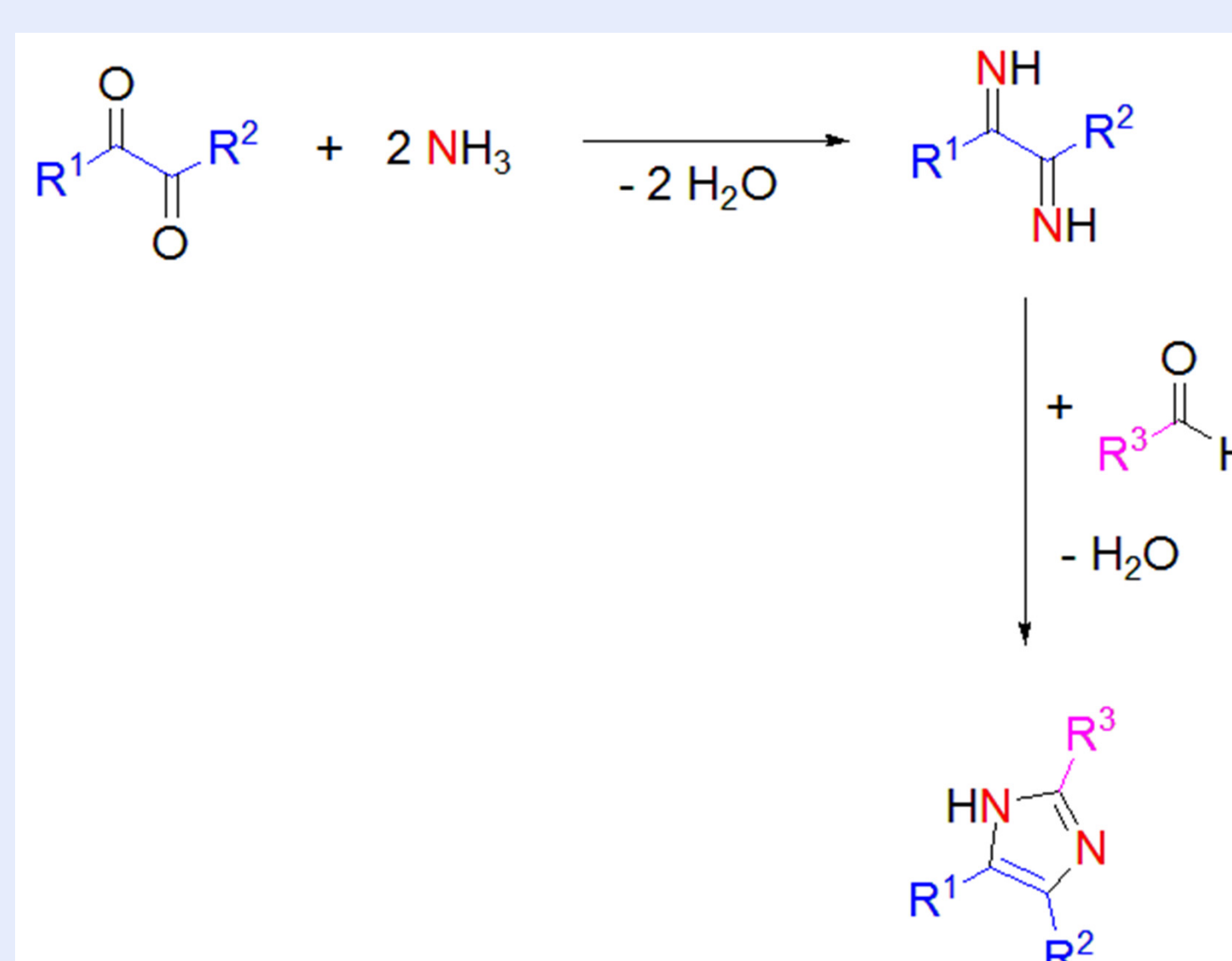**Fig. 1:   UV-spectra of ground state IC. (Yellow background = actinic radiation)**

Fig. 1:   Reaction mechanism (Debus mechanism) of the formation of imidazoles.

OH Radical Kinetics

- Fast reaction of imidazoles with OH radicals
- k_{2nd} comparable with rate constants of OH radical reactions with other aromatic systems
  - → e.g.: pyridine, $k_{2nd, 298K} = 3.0 \cdot 10^9$ M^{-1} s^{-1}
- No temperature dependence in case of IC
- Temperature dependence for other imidazoles
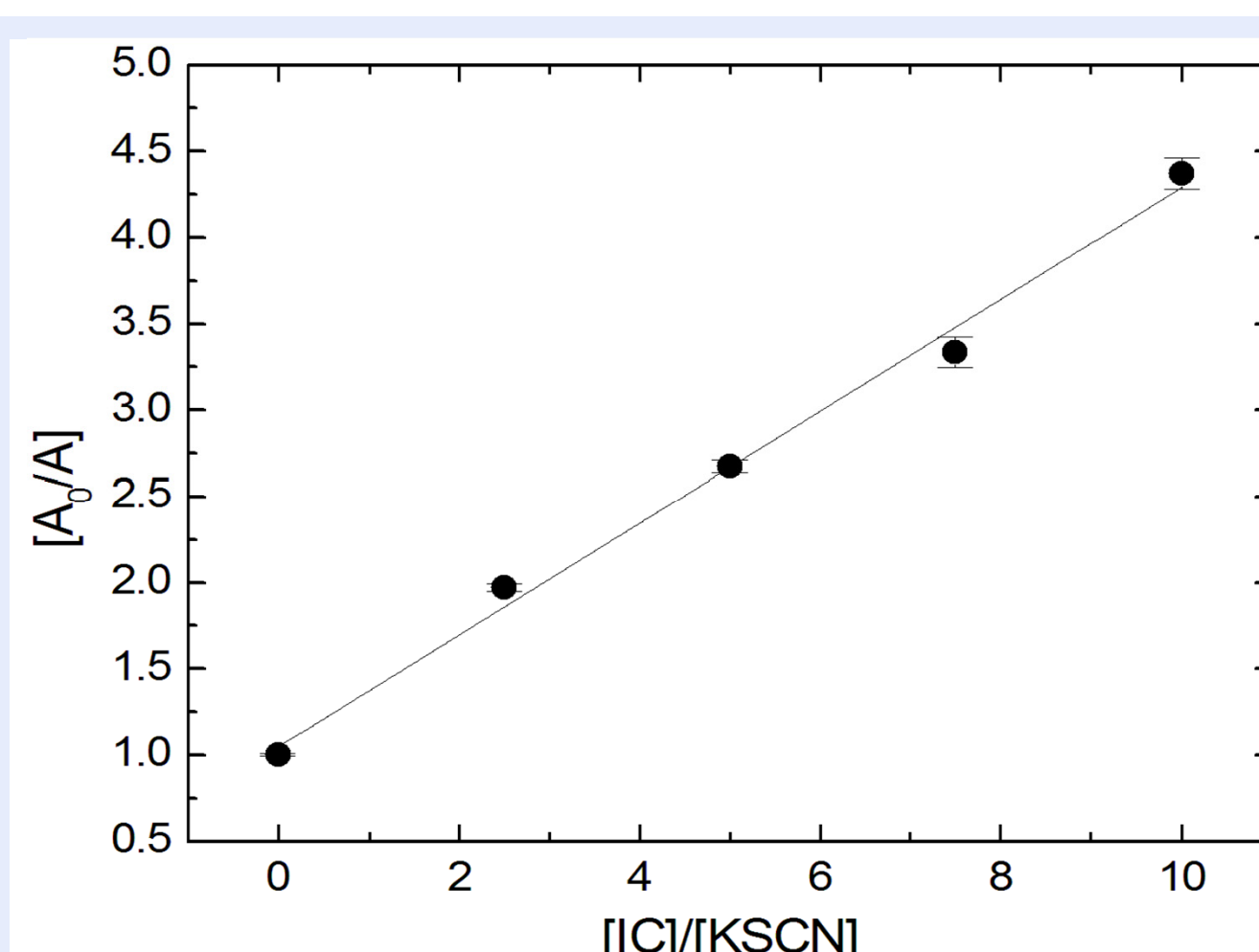 - → Higher temperature = higher k_{2nd}

Fig. 5:   Plot of absorption ratio against concentration ratio for the determination of k_{2nd} at T = 298 K.

T / K	k_{2nd} / 10^9 M^{-1} s^{-1}					
	IC	1-MIHS	2-MI	4(5)-MI	1-EI	2-EI
278	-	2.3 ± 0.3	3.8 ± 0.4	3.8 ± 0.2	2.3 ± 0.2	3.4 ± 0.2
288	3.5 ± 1.4	2.5 ± 0.2	4.7 ± 0.5	4.1 ± 0.4	2.9 ± 0.3	4.2 ± 0.3
293	3.4 ± 1.5	-	-	-	-	-
298	**3.3 ± 1.3**	**2.7 ± 0.2**	**5.4 ± 0.2**	**5.1 ± 0.3**	**3.0 ± 0.3**	**5.0 ± 0.2**
308	3.7 ± 1.3	3.1 ± 0.4	6.6 ± 0.6	6.4 ± 0.6	4.1 ± 0.2	5.7 ± 0.6
318	3.2 ± 1.2	3.6 ± 0.3	9.1 ± 0.7	8.0 ± 0.3	5.2 ± 0.3	6.5 ± 0.9

Compound	$\tau_{aerosol}$ / min	τ_{cloud} / h
IC	12	9
1-MIHS	15	11
2-MI	8	6
4(5)-MI	8	6
1-EI	13	10
2-EI	8	6

$$\tau = \frac{1}{k_{2nd} \cdot [OH]}$$

- Calculation of lifetime τ for urban regions
- $[OH] = 4.4 \cdot 10^{-13}$ mol L^{-1} in aerosol particles
- $[OH] = 1 \cdot 10^{-14}$ mol L^{-1} in cloud droplets
- Possibility to trigger chemistry

Experimental

- Investigation of…
  - … photochemistry of imidazole-2-carboxaldehyde (IC)
  - … hydroxyl (OH) reactions of various imidazoles

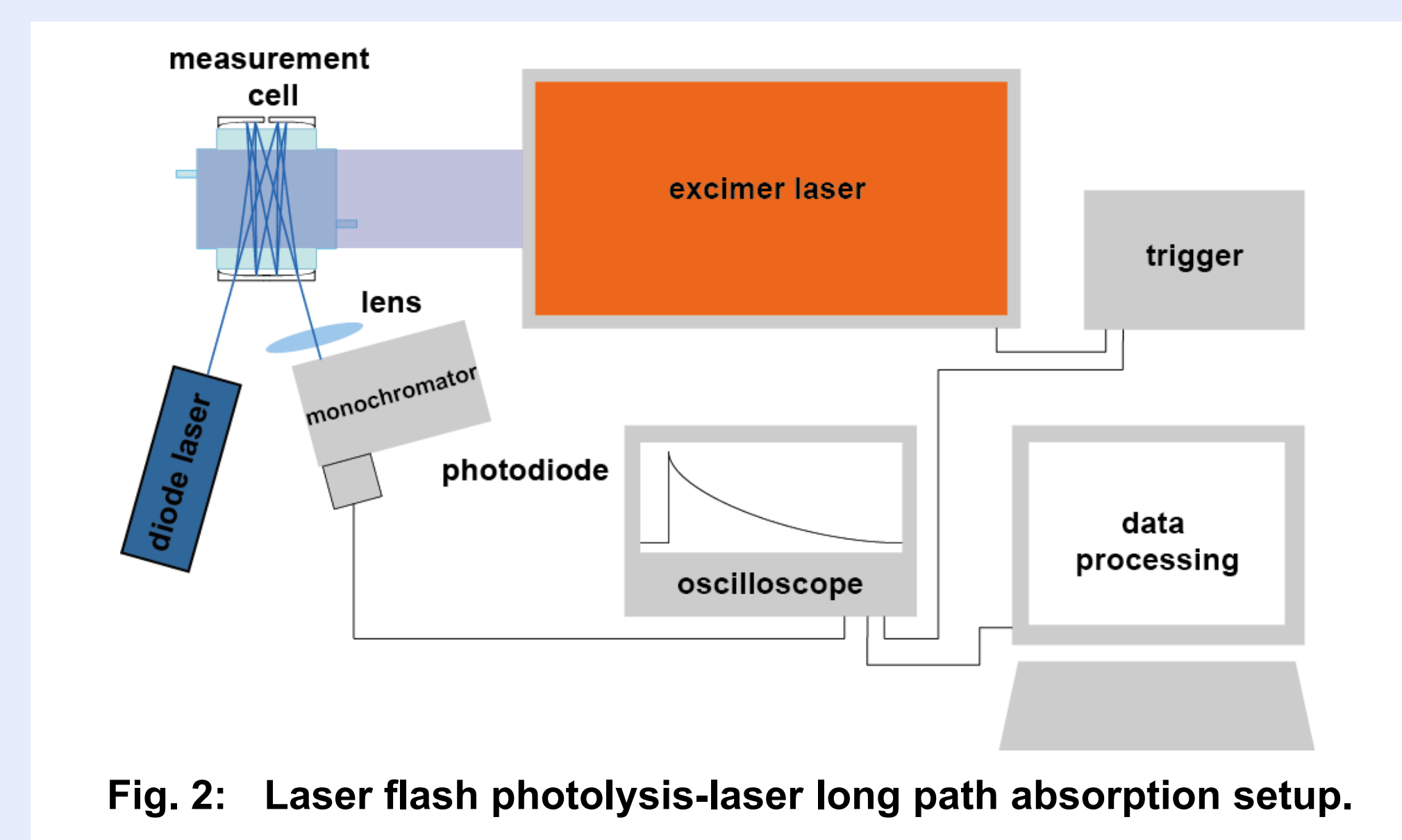| Transient	Precursor compound	$\lambda_{Excimer}$ / nm	$\lambda_{diode\,laser}$ / nm	Reference system
^{3}IC*	IC	308	473	–
OH radical	H_2O_2	248	407	KSCN

Fig. 2:   Laser flash photolysis-laser long path absorption setup.

Results

Quenching Reactions

- Determination of quenching rate constants k_q of excited triplet state IC* with:
  - i.   Bromide anion   → **$k_q = (1.6 \pm 0.3) \cdot 10^7$ M^{-1} s^{-1}**
  - ii. O_2 → **$k_q = (2.5 \pm 0.1) \cdot 10^9$ M^{-1} s^{-1}**
  - iii.   Formic acid   → **$k_q = (8.8 \pm 0.5) \cdot 10^9$ M^{-1} s^{-1}**
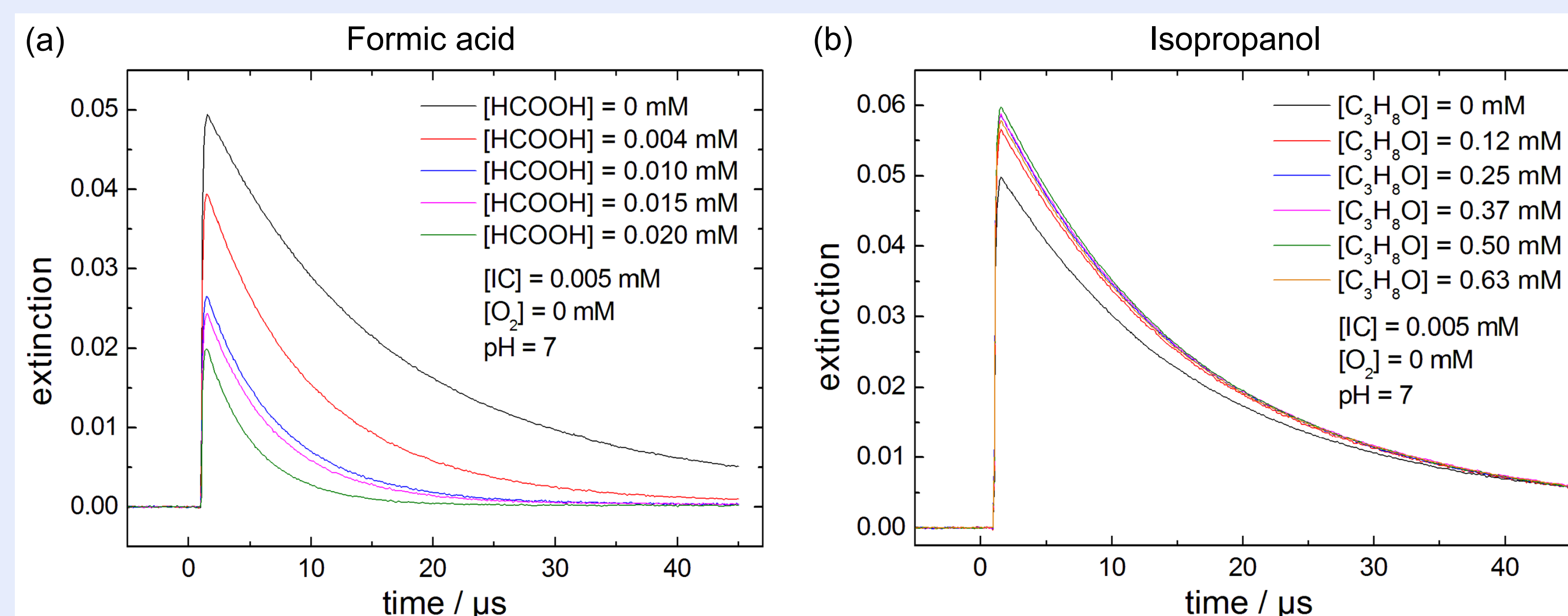 - iv.   Isopropanol   → **k_q not ascertainable**

Fig. 4:   Extinction-time-profiles of the quenching reactions of IC* with (a) formic acid and (b) isopropanol.

- Decrease of IC* controlled by concentration of formic acid
  - Increase of formic acid concentration
    - = increase of first order quenching rate constant k_{1st}
    - = decrease of initial extinction of IC*
- No change of extinction-time-profile by increasing concentration of isopropanol
- Bond dissociation energies (BDE) of C-H-bond of formic acid and isopropanol
  - BDE(C**H**OOH) = 404.2 kJ mol^{-1}
  - BDE((H$_3$C)$_2$C**H**OH) = 380.7 kJ mol^{-1}
    - → **Hydrogen abstraction more favored at isopropanol**
- Change in extinction-time-profile of formic acid not conditioned by hydrogen abstraction
  - → **Assumption: electron transfer**

Summary

- Quenching of IC* with Br⁻ (**$k_q = (1.6 \pm 0.3) \cdot 10^7$ M^{-1} s^{-1}**) lowest reaction
- Quenching of IC* efficiently by O_2 (**$k_q = (2.5 \pm 0.1) \cdot 10^9$ M^{-1} s^{-1}**) and formic acid (**$k_q = (8.8 \pm 0.5) \cdot 10^9$ M^{-1} s^{-1}**)
- Supposed mechanism for photosensitized reactions of IC* with organics: → **electron transfer**
- Fast reaction of imidazoles with OH radicals (**range of 10^9 M^{-1} s^{-1}**)
- Temperature dependence of k_{2nd} for all imidazoles, except IC
- Lifetime of minutes in aerosol particles and hours in clouds
  - → Can trigger chemistry during this time

Outlook

- Further kinetic investigations of photosensitized reactions
  - Other photosensitizers and organic compounds
  - Variation of experimental conditions
- Investigations of photosensitizers concerning their photochemical properties
- Product analysis
- Investigations to the impact of photosensitized reactions
- Implementation of obtained data into model studies

References

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