

Kinetic Studies and Time-Resolved Laser Spectroscopy of Photosensitizers in Tropospheric Aqueous-Phase Chemistry

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Introduction

- Atmospheric loss of organic compounds by...
 - ... Direct photolysis
 - ... Indirect photoinduced or photosensitized processes

• Photosensitized chemistry

- Formation of excited triplet state molecules by solar radiation
- Reaction of excited triplet states with:
 - Inorganic compounds via electron transfer
 - Organic compounds via H-atom abstraction or electron transfer
 - Molecular oxygen via energy transfer

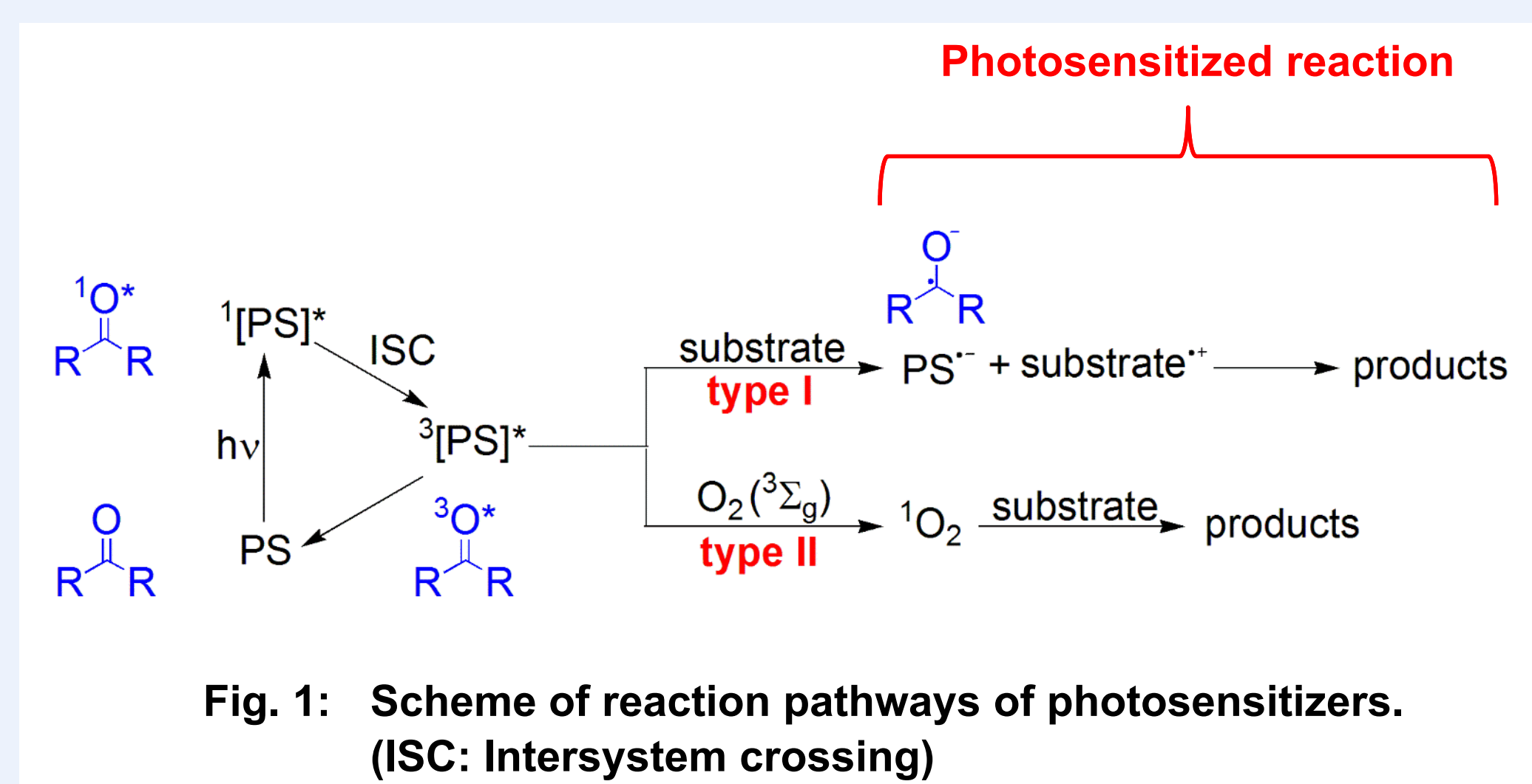


Fig. 1: Scheme of reaction pathways of photosensitizers. (ISC: Intersystem crossing)

- New mechanism of SOA formation based on photosensitized particulate-phase chemistry
- Kinetic data, photochemical properties and mechanisms essential to evaluate the absolute impact of photosensitized reactions in atmospheric particulate-phase

BUT: Data are still scarce!

- Finding suitable compounds which can act as photosensitizers and are atmospherically relevant

Laser flash photolysis-laser long path absorption setup (LFP-LLPA)

Kinetics

- Formation of excited triplet states by photolysis of photosensitizer at $\lambda = 308$ nm
- Analytical light source: continuous wave laser at $\lambda = 473$ nm
- Detector: photodiode
- Determination of rate constants of photosensitized reactions

Spectroscopic

- Formation of excited triplet states by photolysis of photosensitizer at $\lambda = 248$ nm
- Analytical light source: Deuterium lamp & halogen lamp ($\lambda = 200 - 800$ nm)
- Detector: ICCD-camera
- Recording the time resolved absorbance spectra of excited triplet states

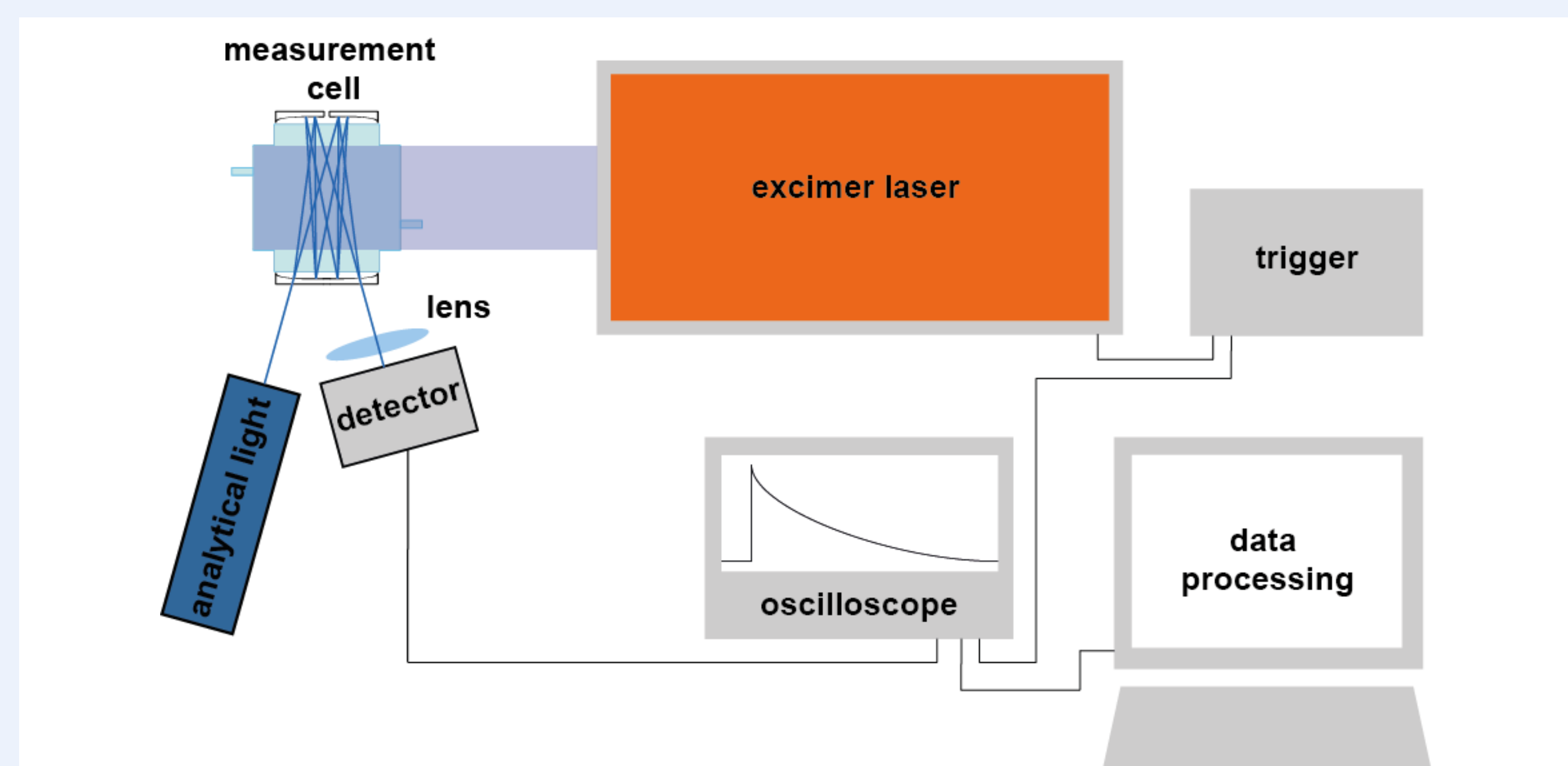


Fig. 2: Laser flash photolysis-laser long path absorption setup (adopted by Otto et al. (2017), *J. Phys. Chem. A*, 121, 6460-6470).

Summary

- Quenching of IC* with Br⁻ ($k_q = (1.6 \pm 0.3) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$) lowest reaction
- Quenching of IC* efficiently by O₂ ($k_q = (2.5 \pm 0.1) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and formic acid ($k_q = (8.8 \pm 0.5) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$)
- Triplet states of IC and BP are formed directly after 100 ns of the laser pulse
 - IC* exists just for a few μs and shows an absorbance maximum at 350 nm
 - BP* has a longer lifetime (up to 240 μs) than IC*
 - BP* shows two absorbance maxima at 325 nm and 540 nm

Outlook

- Further kinetic and spectroscopic investigations
 - Other photosensitizers and organic compounds
 - Variation of experimental conditions (pH, temperature)
- Determination of quantum yields via trapping reactions
- Product analysis
- Investigations to the impact of photosensitized reactions
- Implementation of obtained data into model studies

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Results

Quenching reactions

- Determination of quenching rate constants k_q of excited triplet state of imidazole-2-carboxaldehyde (IC*) with:
 - Bromide anion $\rightarrow k_q = (1.6 \pm 0.3) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$
 - O₂ $\rightarrow k_q = (2.5 \pm 0.1) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$
 - Formic acid $\rightarrow k_q = (8.8 \pm 0.5) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$
- Decrease of IC* controlled by concentration of quencher
 - Increase of quencher concentration = increase of first order quenching rate constant k_{1st}
 - = decrease of initial extinction of IC*

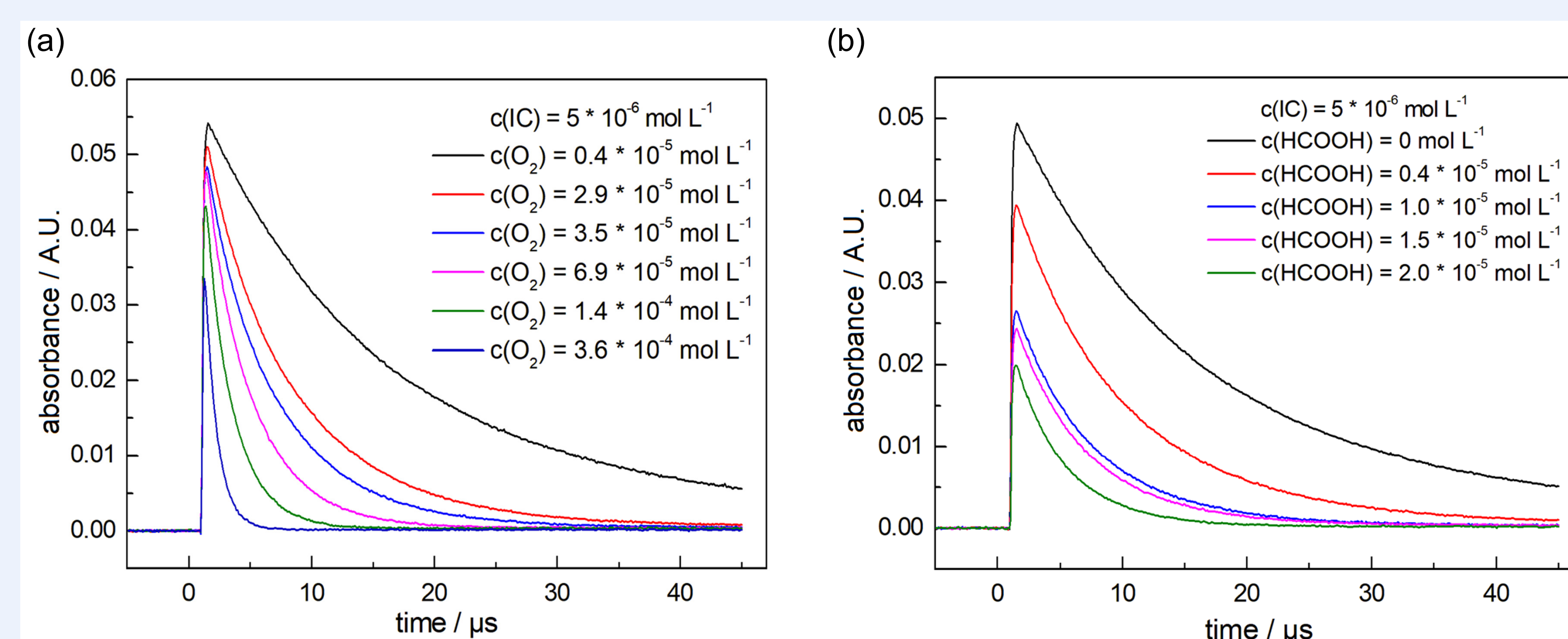


Fig. 3: Extinction-time-profiles of the quenching reactions of IC* with (a) molecular oxygen and (b) formic acid.

Spectroscopy

- Direct formation of excited triplet state of IC* and benzophenone (BP*) after a delay time of 100 ns
- IC* has shorter lifetime (few μs) than BP* (up to 240 μs)
- Absorbance maxima:
 - IC* at about 350 nm
 - BP* shows two maxima: one at about 325 nm and a second at about 540 nm
- Preliminary results of absorbance spectra of BP*

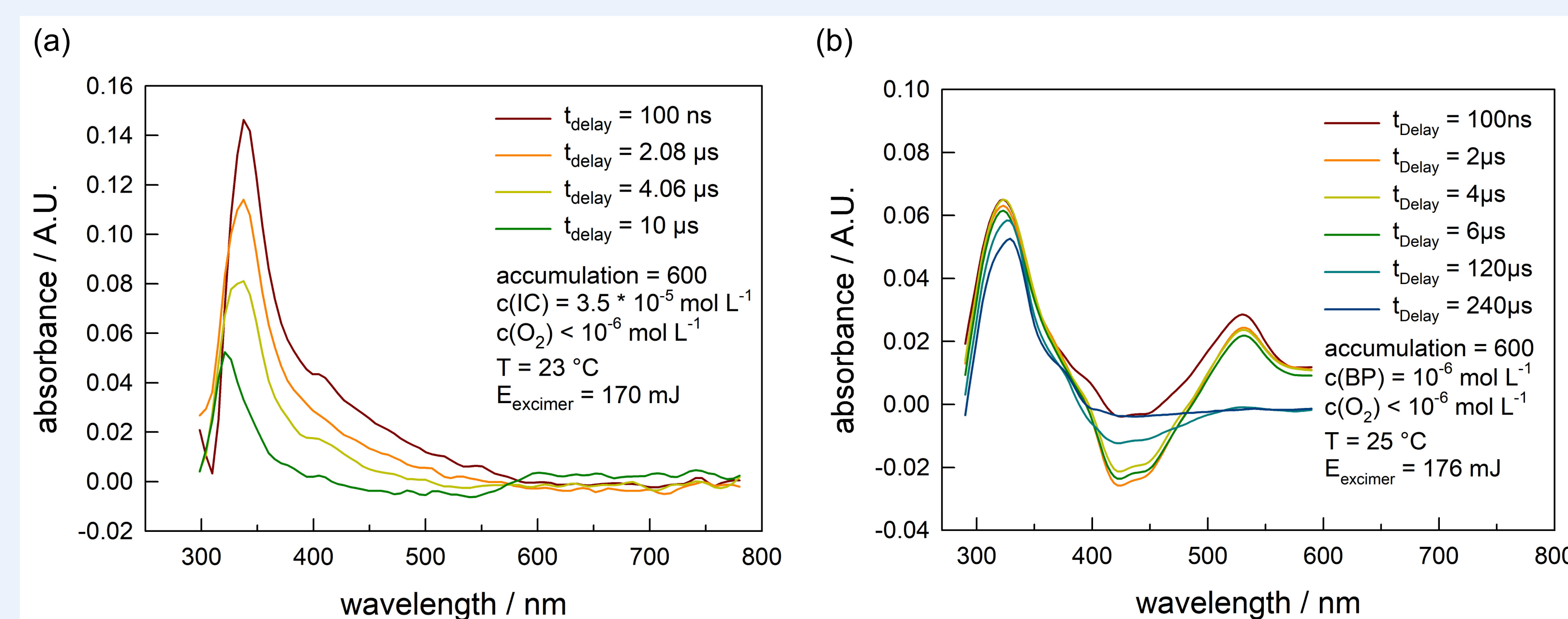


Fig. 4: Time resolved absorbance spectra of excited triplet states of (a) imidazole-2-carboxaldehyd (IC*) at pH = 6 and (b) benzophenone (BP*) at pH = 5.

References

Alvarez et al. (2012), *Environ. Sci. Technol.*, 46, 1955-1963.; Aregahegn et al. (2013), *Faraday Discuss.*, 165, 123-134.; Bensasson (1980), *J.C.S. Faraday I*, 76, 1801-1810.; Cercek et al. (1967), *Trans. Faraday Soc.*, 63, 1687-1698.; Galloway et al. (2009), *Atmos. Chem. Phys.*, 9, 3331-3345.; Herrmann et al. (2010), *Chem. Phys. Chem.*, 11, 3796-3822.; Herrmann et al. (2015), *Chem. Rev.*, 115, 4259-4334.; Kampf et al. (2012), *Atmos. Chem. Phys.*, 12, 6323-6333.; Ledger and Porter (1972), *J. Chem. Soc., Faraday Trans. 1*, 68, 539-553.; Li et al. (2016), *J. Phys. Chem. A*, 120, 9042-9048.; Monge et al. (2012), *PNAS*, 109, 6840-6844.; Otto et al. (2017), *J. Phys. Chem. A*, 121, 6460-6470.; Rossignol et al. (2014), *Environ. Sci. Technol.*, 48, 3218-3227.; Teich et al. (2016), *Environ. Sci. Technol.*, 50, 1166-1173.; Tinel et al. (2014), *C. R. Chimie*, 17, 801-807.; Vione et al. (2006), *Chem. Soc. Rev.*, 35, 441-453.