

Flow Chemistry Highlights

A CHIMIA Column

Review of Recent Literature on Flow Chemistry. Selected Topic: Photochemistry

Flow Photochemistry: Shine Some Light on Those Tubes!

C. Sambiagio, T. Noël*, *Trends in Chemistry* **2020**, *2*, 92, https://doi.org/10.1016/j.trechm.2019.09.003

Implementation of microreactors for light-driven transformations is an excellent example of chemical synthesis benefitting from flow conditions. The transmittance of light decreases exponentially with distance in the bulk of a reaction mixture, causing non-uniform irradiation and forcing long reaction times; small dimensions of the microreactors overcome this issue, improving reaction times and selectivity. In this review, the authors focus on new research directions enabled by performing photochemical transformations in flow. Novel applications include light-driven multiphase reactions or the use of solar energy. The authors have pioneered the utilization of luminescent solar concentrators, which enable down-conversion of the solar energy to drive photocatalytic reactions. Another interesting area is the implementation of automated screening platforms for reaction discovery and optimization. Finally, an overview of most promising scaleup scenarios is presented. The authors also point out the shortcomings of the technology such as handling of solids, generally problematic in microreactors, or limited number of industrially relevant scale-up demonstrations to date.

Author's comments*:

"The impact technology makes is directly correlated with how deep it is embedded in a certain field. It is fair to say that the use of flow reactors for photochemical transformations is one of the most successful examples in flow chemistry."

100 Round-bottom flask Microcapillary ID < 1 mm Vial ID > 1 cm ID > 2.5 - 3 cm80 Transmittance (% 60 40 Increasing 20 conc 0.5 1.0 1.5 2.0 Distance

(F) Attenuation of light irradiance with distance

Organophotocatalytic Aerobic Oxygenation of Phenols in a Visible-Light Continuous-Flow Photoreactor

J. Wellauer, D. Miladinov, T. Buchholz, J. Schütz, R. T. Stemmler, J. A. Medlock, W. Bonrath, C. Sparr*, *Chem. Eur. J.* **2021**, *27*, 9748, https://doi.org/10.1002/chem.202101313

Quinones are key intermediates in numerous industrially relevant targets which include vitamins E and K₂. The result of an academic-industrial collaboration, the authors describe a mild and general access to quinones from phenols by employing aerobic conditions in the presence of the readily available photocatalyst methylene blue and a visible LED light source. Continuous flow conditions are used to provide a platform able to tune multiple variables, the ability of working under 10 bar pressure, and for reasons of safety. Various insights are shared, such as the effect of light filters, and light sources with narrow emission bands in order to avoid benzoquinone product degradation. The result is a general flow method to quinones which also includes naphthol oxygenations under the same conditions, as well as *para*-quinols after thiosulfate reduction in batch. A gram-scale synthesis of a substituted benzoquinone in nearly quantitative yield rounds off the study.

Author's comments*:

"This collaboration between DSM Research Kaiseraugst and the Sparr group of the University of Basel aimed at a sustainable, highyielding aerobic phenol oxygenation as alternative to problematic Cu-based processes. A suitable flow reactor design, LED light, air overpressure, low amounts of an organic photocatalyst and a benign solvent allowed very selective oxygenations with up to 99% yield."

