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EXPERIMENTAL METHODOLOGY TO MEASURE THE REACTION RATE CONSTANTS OF PROCESSES SENSITIZED BY THE TRIPLET STATE OF 4-CARBOXYBENZOPHENONE AS PROXY OF THE TRIPLET STATES OF CHROMOPHORIC DISSOLVED ORGANIC MATTER

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By combination of transient absorption spectroscopy (Laser Flash Photolysis) and steady-state irradiation experiments, we investigated the transformation of phenol and furfuryl alcohol (FFA) sensitized by irradiated 4-carboxybenzophenone (CBBP). The latter is a reasonable proxy molecule to assess the reactivity of the excited triplet states of the chromophoric dissolved organic matter (³CDOM*) that occurs in natural waters and that plays often an important role in the photochemically activated self-depollution ability of water bodies.[1,2] The main reactive species for the transformation of both phenol and FFA was the CBBP triplet state (³CBBP*), despite the fact that FFA is a commonly used probe for singlet oxygen (¹O₂). In the case of FFA it was possible to develop a simple kinetic model that fitted well the experimental data obtained by steady-state irradiation, in a wide range of FFA concentration values. The GC-MS analysis carried out with a SPME fiber coated showed that furfural was the only detected FFA transformation intermediate. In the case of phenol the model was made much more complex by the likely occurrence of back reactions [2] between radical species (e.g., phenoxyl and superoxide). This problem can be tackled by considering only the experimental data at low phenol concentration, where the degradation rate increases linearly with concentration.

We do not recommend the use of ¹O₂ scavengers/quenchers such as sodium azide to elucidate CBBP photoreaction pathways, because the azide provides misleading results by also acting as a triplet state quencher. Based on the experimental data, we propose a methodology for the measurement of the CBBP triplet-sensitization rate constants from steady-state irradiation experiments, allowing for a better assessment of the triplet-sensitized degradation of emerging contaminants in irradiated natural waters.

[1] D. Vione, M. Minella, V. Maurino, C. Minero, Indirect photochemistry in sunlit surface waters: Photoinduced production of reactive transient species. *Chem.-Eur. J.* 20 (2014) 10590-10606.

[2] B. Koehler, F. Barsotti, M. Minella, T. Landelius, C. Minero, L. J. Tranvik, D. Vione. Simulation of photoreactive transients and of photochemical transformation of organic pollutants in sunlit boreal lakes across 14 degrees of latitude: A photochemical mapping of Sweden. *Water Res.* 129 (2018) 94-104.

[3] D. Vione, D. Fabbri, M. Minella, S. Canonica. Effects of the antioxidant moieties of dissolved organic matter on triplet-sensitized phototransformation processes: Implications for the photochemical modelling of sulfadiazine. *Water Res.* 128 (2018) 33-48.