

Mechanistic Studies of Photoredox Organocatalysis by Transient Absorption Spectroscopy and Precise Quantum Yield Determination

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Recently photoredox catalysis merged with organocatalysis has been proven to be a very powerful technique for some elusive chemical transformations, e.g., α -alkylation of aldehydes.^[1] Nevertheless, a mechanistic explanation with spectroscopic evidence for these reactions is still lacking.^[2] It is widely believed that the systems are too complex to be studied with transient absorption (TA) spectroscopy.^[3] We now go beyond this belief by reporting a detailed investigation of α -alkylation of octanal with the photocatalyst naphthalendiimide (NDI) and the organocatalyst imidazolidinone. By using the TA spectrometer of our own design^[4], we track the generation and quenching of the NDI singlet, triplet excitation and radical anion under selective influence of the individual reactants in catalysis from ps to μ s. An example of the study of the productive pathway via electron transfer in the catalysis is shown in Fig. 1.

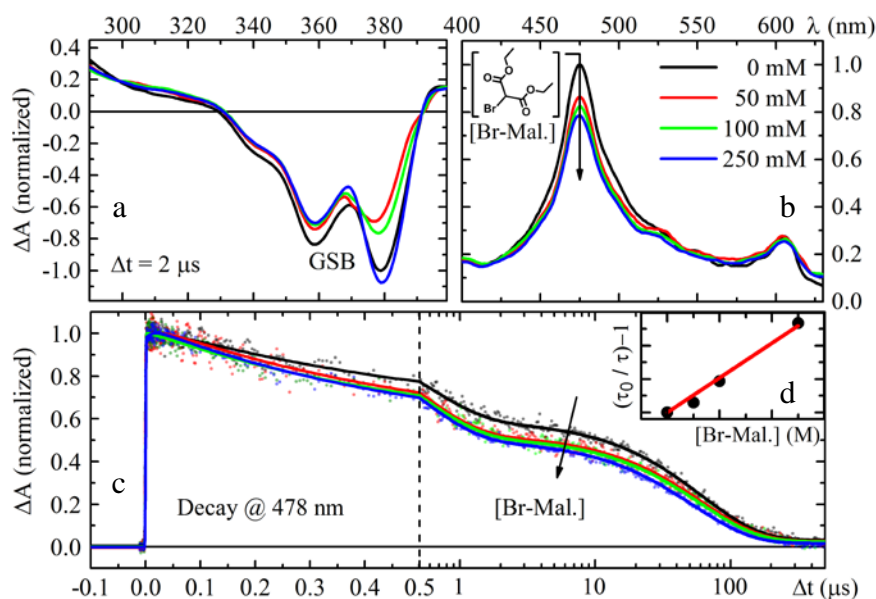


Figure 1. a) and b) Transient absorption of NDI radical anion for different diethyl- α -bromomalonate (Br-Mal.) concentrations at 2 μ s delay. c) Decay of the transient absorption of NDI radical anion. d) Quenching of NDI radical anion by the Br-Mal.

At wavelength below 400 nm the ground state bleach allows us to quantitatively determine the concentration of excited catalyst and by its recovery the completion of the catalytic cycle. The peak at 478 nm is readily assigned to the NDI radical anion. Following its appearance and eventual disappearance directly monitors the NDI anion concentration.

By using the LED based quantum yield determination system of our own design (QYDS)^[5], we reproduce the quantum yield (QY) result that was reported by Yoon^[6] for Ru(bpy)₃²⁺ catalyzed α -alkylation of octanal. They report a QY of 1800 % and concluded a radical chain

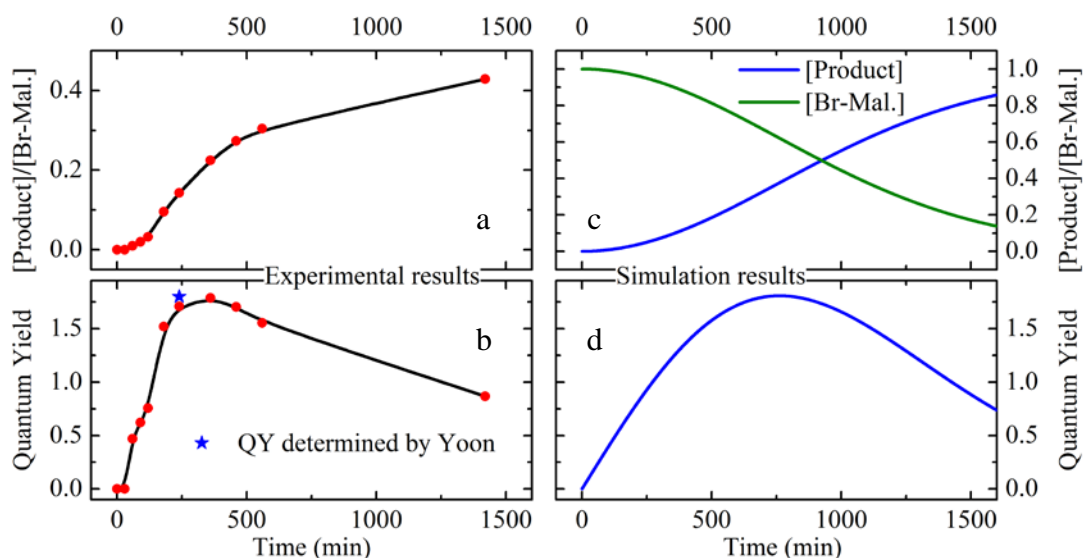


Figure 2. The time dependence of product concentration and the reaction quantum yield for Ru(bpy)₃²⁺ catalyzed α -alkylation of octanal. a) and b) are the results from QYDS, c) and d) are the simulation results of our model.

mechanism. However, we find that the QY of this reaction depends strongly on irradiation time and doesn't remain > 100 % throughout. We suggest a mechanism that combines photocatalysis and radical chain reaction. A first simulation according to this model is shown in the Fig. 2. During the quantitative reaction needed for a good chemical yield, the substrate concentration is strongly changed and any diffusive mechanism involving the substrate and possibly intermediates will change in importance. At the same time, the possible aggregation equilibrium will also be influenced.

As a general consequence we suggest that the simple definition of the quantum yield valid for a unimolecular photophysical process like fluorescence cannot be directly transferred to photochemical or photocatalytic processes. A more complete description is needed and the momentary QY given by the differential amount of product produced a given amount of light should be reported as a function of irradiation time and illumination strength.

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