

NMR spectroscopic investigations of the hydrogen bond induced photocatalytic hydroamidation of *N*-arylamides

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The catalytic olefin hydroamidation is an efficient process to generate biologically active nitrogen-containing compounds without prefunctionalization of the amide substrate.^[1]

In 2015, Knowles *et al.* published an optimized catalyst system for the photocatalytic intramolecular hydroamidation of unactivated aryl amide derivatives. In this report, the amide was transferred into an amidyl radical via proton-coupled electron transfer (PCET) by using an excited iridium photocatalyst and a Brønsted base. Subsequent olefin addition using thiophenol as the most effective hydrogen-atom donor generates the cyclic product. Surprisingly, the amide substrate was selectively transferred into the radical in presence of thiophenol although the N-H-bond (99 kcal/mol) is much stronger than the S-H-bond (79 kcal/mol). The postulated explanation is a difference in hydrogen bond donor abilities of the amide and thiol with the N-H functionality being a better donor. Hence, a stronger interaction between amide and Brønsted base is formed resulting in an efficient activation of the substrate.^[2,3,4]

In order to investigate the hydrogen bond donor abilities of the published amide and thiol functionalities, the system consisting of ¹⁵N-labeled *N*-phenylpent-4-enamide, thiophenol and tetrabutylammonium di-*tert*-butyl phosphate was investigated by low temperature NMR spectroscopy. Through the chemical shift and coupling constant analysis of ¹H, ¹⁵N and ³¹P-NMR spectra a strong N-H···O-P hydrogen bond between amide and Brønsted base was observed without a significant change in presence of thiophenol.^[5] These findings might support the postulated hydrogen bond generation between the amide substrate and the phosphate base by Knowles *et al.* as the reason for the unexpected transformation of the N-H functionality. However, 2D NOESY and DOSY experiments indicate the formation of a supramolecular aggregate between the three species revealing an additional possibility for the selective N-H activation.

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