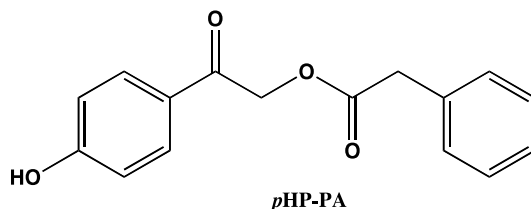


Abstract

p-Hydroxyphenacylphenylacetate: Can the Release Quantum Yield be Increased?

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Photoremovable protecting groups (PPGs) are a key tool for investigation of biochemical processes in living cells due to their ability to release the substrates in time and space of interest.^{1,2}

p-Hydroxyphenacyl moiety has been proved to be an efficient photoremovable protecting group (PPG) for various substrates, for example, halides, phenols and acids. The mechanism of their photodeprotection involves a rapid ISC to the triplet state followed by a subsequent release of the substrate and concomitant formation of a triplet biradical that closes to the putative spirodione intermediate. Hydrolysis of the putative spirodione intermediate formed *p*-hydroxyphenylacetic acid.³ The release of good leaving groups such as diethyl phosphate, tosylate and mesylate, was efficient with high quantum yields (~ 1) and ultrafast release rates ($k \sim 10^{10} \text{ s}^{-1}$). However, the quantum yield drops significantly for poor leaving group (~ 0.05 for phenol). An adiabatic triplet state tautomerization⁴ might represent the energy wasting paths decreasing the quantum yield of the *p*HP PPG.

In the present work, we studied how the concentration of a general base and pH (acetate buffer at pH 3.6 and 6) affects the overall disappearance quantum yields of *p*HP phosphate. Five different phenyl ring substituted *p*HP-PA derivatives have also been synthesized to investigate the effects of phenyl ring substituents to the overall quantum yields. The results were correlated with those of laser flash photolysis and quantum chemical calculations.

¹ Wirz J., *Photochem. Photobiol. Sci.*, 2012, 11, 445

² Klán P., Šolomek T., Bochet C., Blanc A., Givens R. S., Rubina M., Popik V., Kostikov A., Wirz J. *Chem. Rev.* 2013, 113, 119–191.

³ Givens R. S., Heger D., Wirz J., *J. Am. Chem. Soc.* 2008, 130, 3307, and references therein.

⁴ Klíčová L., Sebej P., Solomek T., Hellrung B., Slavíček P., Klán P., Heger D., and Wirz J., *J. Phys. Chem. A* 2012, 116, 2935–2944