Proton-coupled electron transfer in the reduction of carbonyls using SmI_2-H_2O : implications for the reductive coupling of acyl-type ketyl radicals with SmI_2-H_2O.

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Streszczenie

Samarium diiodide–water (SmI_2–H_2O) reagents have emerged as some of the most practical systems enabling reduction and reductive cyclizations of ketyl radicals. Recently, this reaction manifold has been extended to acyl-type radicals generated from cyclic polar carboxylic acid derivatives. However, the relationship between the fundamental electron- and proton-transfer steps in the generation of ketyl-type radicals with SmI_2–H_2O remains unclear. An intriguing scenario involves an initial proton-coupled electron transfer (PCET) mechanism from SmI_2–H_2O to the carbonyl group. Herein, we calculate with high accuracy bond dissociation free energies (BDFE) for the O–H bond in ketyl radicals in 14 cyclic and acyclic ketone, ester, imide and amide substrates and in anthracene relevant to reductions with SmI_2–H_2O and quantitatively assess the feasibility of concerted PCET in the reduction of carbonyl groups using SmI_2–H_2O. Reduction potentials of all substrates have been calculated. The data argue against concerted PCET from SmI_2–H_2O to carbonyl substrates.

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