Solvent effect on kinetics and mechanism of the phospha-michael reaction of tertiary phosphines with unsaturated carboxylic acids

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Abstract

In aprotic solvents, kinetics of the reaction of triphenylphosphine with acrylic acid is second order in the acid and first order in the phosphine. To find the most suitable model to describe the solvent effect on this reaction, the third-order rate constants in a series of 16 aprotic solvents were analyzed using one- and multiparameter regressions within the framework of the Kamlet-Taft, the Catalán, the Gutmann-Mayer, and the Koppel-Palm equations. The best result gives a two-parameter model constructed on the basis of the Reichardt polarity ET and the basicity B from the Koppel-Palm equation, with the weak positive effect of the ET parameter on the reaction rate and very strong negative effect of the B parameter. The results obtained give further evidence to the previously suggested a stepwise mechanism, which involves the initial formation of a zwitterionic intermediate, followed by the proton transfer from the second molecule of acrylic acid to the generated carbanionic center in the rate-determining step. © 2014 Wiley Periodicals, Inc.