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Quantum chemical investigation on the reaction mechanism of tertiary phosphines with unsaturated carboxylic acids: An insight into kinetic data

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Abstract

The structures of intermediates and transition states in the reaction of tertiary phosphines with unsaturated carboxylic acids have been calculated at the B3LYP level of theory using the 6-31+G(d,p) basis set. Analysis of the results shows that [1,3]-intramolecular migration of carboxylic proton to carbanionic center of generated zwitterionic intermediate is strongly kinetically unfavorable, and external proton-donor source is essential to complete quaternization. A molecular cluster of the intermediate with one molecule of water has been modeled for intermolecular reaction pathway, but even in this case, the proton transfer remains to be the rate-determining step that is in a good agreement with previous kinetic investigations on this reaction. The data obtained for this reaction have much in common with recent studies on the mechanisms of the Morita-Baylis-Hillman reaction and phosphine-catalyzed [3+2] cycloaddition, which revealed paramount importance of proton-transfer steps. Copyright © 2012 Wiley Periodicals, Inc.

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Keywords

density functional theory, intermediates, intrinsic reaction coordinate, molecular cluster, proton transfer, tertiary phosphines, transition state, zwitterions