عنوان مقاله:

Experimental and Theoretical Study on the Mechanism and Kinetics of the Reaction between Hexamethyl Phosphorous Triamide and Dialkyl Acetylenedicarboxylates in the Presence of Benzimidazole

محل انتشار:

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خلاصه مقاله:

The study examined the reactions of hexamethyl phosphorous triamide (HMPA) ۱, dialkyl acetylenedicarboxylates ۲, and benzimidazole ۳ (NH-acids) by conducting comprehensive kinetic analyses. Kinetics and mechanistic analysis of the reaction were investigated using theoretical and experimental methods. UV-Vis technique was employed to track experimental data whereas ab initio was employed to investigate theoretical studies revolving around the carbon-carbon double bond (OCH۳-C C-P (NMe۲)۳) in phosphorus ylides ۴a-b. Using UV-Vis spectrophotometry, the second-order fits were automatically drawn, and the second-order rate constants (k۲) were computed by the standard equations within the program. Calculations were made for the reaction's activation energy and parameters (Ea, DH#, DS# and DG#). Likewise, the gathered data on how the solvent, reactant structure, and reactant concentration affected reaction rates. The suggested mechanism was verified through experimental data and the steady state approximation, the rate-determining step (RDS) found to be the first and the third steps (k۲ and k۳). Three proposed mechanisms were hypothesized through quantum mechanical calculations. However, the second and the third mechanisms did not match with the experimental data, while the first mechanism showed agreement between theoretical and experimental kinetic data. It was found that the HF/۶-۳۱G (d, p) basis set provided more accurate results for compound ۴a than the B۳LYP/۶-۳۱G (d, p) basis set did, whereas the latter performed better for compound ۴b.

کلمات کلیدی:

Kinetic parameters, UV/Vis spectrophotometery, Theoretical Kinetics, Hexamethyl Phosphorous Triamide, Dynamic ۱H NMR