Electrocyclic [1,5] Hydrogen Shift in the Thermal Elimination Kinetics of Phenyl Acetate and p-Tolyl Acetate in the Gas Phase: A Density Functional Theory Study.

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The kinetics and mechanisms of thermal decomposition of phenyl acetate and p-tolyl acetate in the gas-phase were studied by means of electronic structure calculations using Density Functional Theory (DFT) methods: B3LYP/6-31G(d,p), B3LYP/6-31++G(d,p), B3PW91/6-31G(d,p), B3PW91/6-31++G(d,p), MPW1PW91/6-31G(d,p), MPW1PW91/6-31++G(d,p)], PBE/6-31G(d,p), PBE/6-31++G(d,p), The examination of the reaction pathways considered two possible mechanisms. Mechanism A, is stepwise involving electrocyclic [1,5] hydrogen shift to eliminate ketene through concerted six-membered cyclic transition state structure, followed by tautomerization of cyclohexadienone or 4-methyl cyclohexadienone intermediate product to give the corresponding phenol. Mechanism B is one-step concerted [1,3] hydrogen shift through four-membered cyclic transition state geometry, to produce ketene and phenol or p-cresol. Theoretical calculations showed good agreement with experimental activation parameters for phenyl acetate, using the PBE functional, through the stepwise mechanism. For mechanism B large deviation for the entropy of activation was observed. No experimental data was available for p-tolyl acetate; however, theoretical calculations showed similar results to phenyl acetate, thus supporting the stepwise mechanism for both phenyl acetate and p-tolyl acetate.

Keywords: phenyl acetate, p-tolyl acetate, density functional theory, gas-phase elimination kinetics and mechanisms