DFT and Ab-initio studies on the reaction mechanism of the homogeneous, unimolecular elimination kinetics of selected 1-chloroalkenes in the gas phase

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The mechanisms for the unimolecular elimination kinetics of selected 1-chloroalkenes in the gas phase were studied at MPW1PW91/6-31G(d,p), MPW1PW91/6-31++G(d,p), G3 and G3MP2 levels of theory. Two possible unimolecular mechanisms were considered: Mechanism A as a concerted 1,2 elimination process through four-membered cyclic transition state. Mechanism B describing the anchimeric assistance of the double bond in HCl elimination previously suggested in the literature. Calculated parameters suggest the elimination reactions of 1-chloroalkenes proceed through Mechanism A, in view of the higher energy of activation associated with Mechanism B. Density functional method MPW1PW91/6-31G (d,p) calculated parameters gave better agreement with the experimental values than G3 and G3MP2. The changes along the reaction path of Mechanism A were followed by geometric parameters, NBO charges, and bond order analysis, suggesting the rate-determining process is the breaking of C-Cl bond in the transition state. The dehydrochlorination of chloroalkenes occurs in a concerted non-synchronous fashion with stabilization of the transition state by π-electron delocalization from the neighboring bond. Isomerization reactions for 4-chloro-1-butene, 4-chloro-2-methyl-1-butene, and 4-chloro-1-butene are unlikely at the experimental reaction condition because of the higher the enthalpies and energies of activation.

Keywords: 1-chloroalkenes, mechanism, elimination kinetics, density functional theory (DFT), G3 and G3MP2 methods